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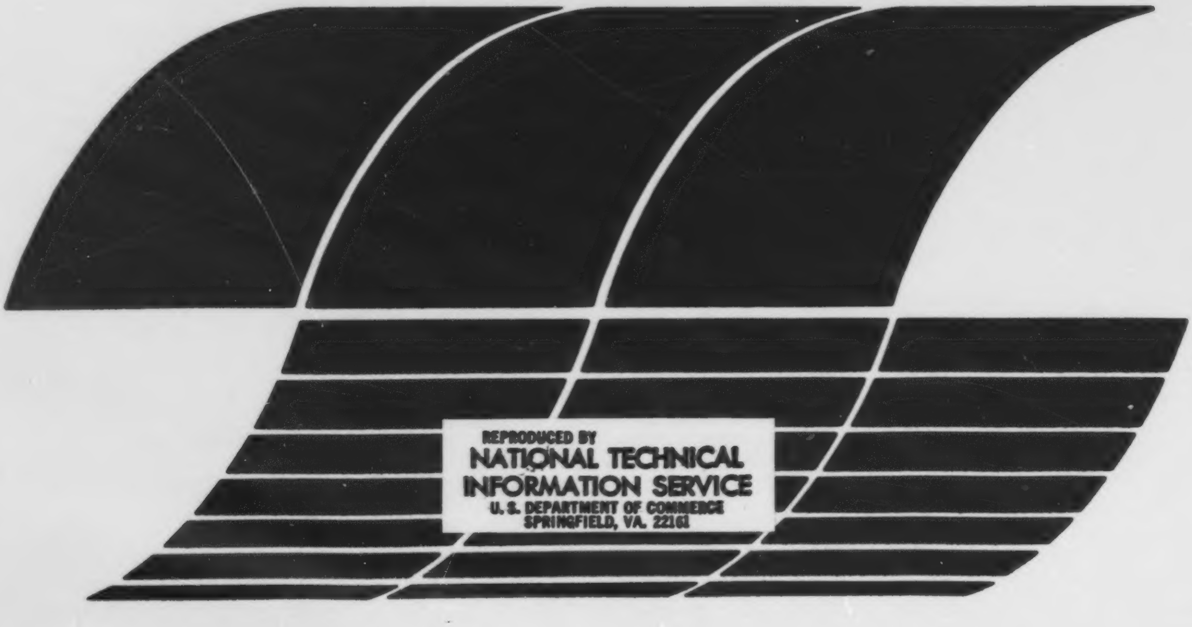

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TRW Systems Group
One Space Park
Redondo Beach, California 90278

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EPA Project Officer: Ronald A. Venezia

Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
Research Triangle Park, NC 27711

Prepared for

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ABSTRACT

This manual describes a detailed and integrated set of sampling and analytical procedures for conventional combustion sources which are compatible with the information requirements of a comprehensive Level 1 environmental assessment. The purpose of the data to be generated by these tests is to ultimately provide emission factors for conventional stationary combustion sources.

This is the first detailed application of Level 1 procedures to all phases (sampling, sample handling, disbursement, and analysis) of a specific program. Although this manual has been designed to meet the exact data needs of this program, the procedures have general applicability to most environmental assessment activities. Specific chapters are included for quality assurance, sample and data management, field sampling, field analysis, organic analysis, and inorganic analysis.

PREFACE

This procedures manual has been prepared for the Industrial and Environmental Research Laboratory, Chemical Processes Branch, Research Triangle Park, North Carolina, as required by EPA Contract 68-02-2179 for Emissions Assessment of Conventional Combustion Systems. Dr. Ron Venezia is the Project Officer at CPB and Mr. Birch Matthews is Program Manager at TRW.

The manual was originally designed to be an internal working document for TRW and its subcontractors. However, because it is the first detailed application of Level 1 procedures on a specific program requiring the sampling of a large number of sites and analysis of a large number of samples, it was decided to publish it as an official EPA document. This process required the interpretation of sometimes conflicting requirements and the addition of procedural details not supplied in the Level 1 manual. In some cases, development work was performed to reduce the procedures to practice. Some of this work has been incorporated into the revised Level 1 manual and some remains specific to this program. These changes are documented in detail in the latter part of this section.

The objective of this project is to assess air and water pollutants generated by conventional stationary combustion systems including those pollutants generated from related solid waste disposal. The final assessment will be based upon appropriate existing emissions data as well as new data acquired through source sampling and analysis. To accomplish this objective, the project scope of work includes the following activities:

1) Define criteria for determining the adequacy of existing emission data.
2) Identify emission source categories or category portions which have been adequately assessed based upon the developed criteria.
3) Specify those source categories that require additional investigation.
4) Develop a test program to complete the emissions assessment.
5) Implement the test program and complete the emissions assessment.

The procedures are designed to be an integral part of the phased environmental assessment approach and apply primarily to Level 1. The purpose of the initial phase is to obtain preliminary environmental assessment information, identify problem areas and provide the basis for the prioritization of streams, components and classes of materials for further testing by more stringent techniques and procedures. As such, the results of the sampling and of the corresponding analysis procedures are quantitative within a factor of ± 2 to 3. A detailed discussion of the approach along with the criteria used for method selection is given in the IERL-RTP Document # EPA-600/2-76-160a, IERL Procedures Manual: Level 1, Environmental Assessment, which has been the guideline for preparation of this document and by reference, is made an integral part of it.

Level 2 sampling and analysis has not been systematically addressed in the manual because it is impossible to predict how the Level 1 results of this program will affect the need for Level 2 analysis. Consequently, Level 2 sampling and analysis plans will be submitted as these requirements are made known. In the cases of polynuclear aromatic hydrocarbons (POM), and sulfate compound determinations, Level 2 needs are presently delineated and consequently procedures are included for sampling and analysis of these materials.

The manual has been designed to fit the specific sampling and analysis requirements for this program although it is recognized that the procedures are general enough to be modified easily for EPA activities relating to other emission sources. In order to avoid confusion, project related deviations are listed in Table i. In addition to these, revisions have been made during the course of the program to reflect experience, changing data needs and EPA directed Level 1 changes. These are listed in Table ii.

Table i. Program Related Additions and/or Deletions to Level 1 Procedures

Parameter/Analysis of Interest	Change and Reason	Section Number
Polynuclear Organic Material	Added as program requirement.	3.4.2 7.10
Polychlorinated Biphenyls	Added as program requirement, deleted from this revision because of uniformly negative results on other programs.	3.4.1
Controlled Condensation System (CCS)	Added to obtain particulate sulfate, aerosol H_2SO_4, and SO_2 information unavailable from Level 1 procedures.	3.3.3 5.6 8.8
Bacharach Smoke Spot Test	Added as program requirement.	6.7
Cyclone Deletion Guidelines	Added to save leak check and clean-up time in field when previous data indicates a cyclone catch will be nil. Updated to increase capability with EPA's fine particulate data bank in September, 1978.	3.3.1 5.2.8
Duty Cycle Testing	Added to answer questions on the effect of the duty cycle and emissions level in residential sources.	3.3.2
Chloride and Fluoride	Added - these elements are often difficult to analyze by SSMS. A set of analysis was developed to check SSMS data in selected cases.	3.4.3 8.9 8.10
BOD and COD	Dropped for cooling and ash quenching stream because of known promlems in interpreting results.	----
Fugitive Emission Studies	Reduced because sufficient data input is being generated by other EPA programs.	3.4.6
Speciation in Bulk TCO Analysis	Added to provide data concerning individual C_7-C_{16} species for OAQPS	7.7
Parr Bomb Combustion	Modified by addition of a quartz liner to reduce blanks. Accepted as official Level 1 change.	8.2.1
Hg, As, Sb Wet Chemical Analysis	Modified or method changed when reduced to practice. All changes accepted as official Level 1 changes.	8.4 8.5 8.6
Water Sampling and Analysis	Reduced to fit actual data needs of program. Directed change June, 1978.	3.8
Ash Sampling and Analysis	Reduced to fit actual data needs of program. Directed Change June, 1978.	
Computation of Inorganic Emissions from Oil and Gas Fired Units	Modified to assume that inorganic emissions are nil from gas fired sites and to assume that all inorganics in fuel are emitted from the stack. Directed change June, 1978.	3.9 7.1 8.1
Deletion of SASS Inorganic Analysis on Gas and Oil Fired Sites	Deleted because very low particulate loadings did not give technically acceptable results. Directed change June, 1978.	3.9 7.1 8.1
Combination of all Organic Samples for a Single Analysis for Oil and Gas Fired Site	Modified so that the XAD-2 extract and all rinses are combined into a single sample because of very low levels of organics in all samples except XAD-2 extract. Directed change June, 1978.	3.9 7.1
Inorganic (Field) Gas Analysis	Modified to a two column Molecular Sieve 13X and Chromosorb 102 system so that all species of interest can be analyzed properly.	6.2

Table ii. Modification and EPA Directed Changes to Level 1 Procedures.

Parameter/Analysis of Interest	Change and Reason	Date	Section Number
Field Analysis for Gaseous Species	Original Level 1 procedures still in use.	----	6.2
Impingers	The use of isopropyl alcohol to wash out impinger bottles was dropped because excessive amounts sometimes interfered with AA analysis.	8/77	5.2.11
Probe, Cyclone, and XAD-2 Module Rinses	Acetone was substituted for methanol because water could not be removed from methanol easily and TCO loss during concentration.	9/77	5.2.11
SASS Train Passivation Procedure	Changed to a 15% HNO_3 soak for 30 minutes to reduce SASS train corrosion. Official Level 1 change.	6/77	5.2.6
First H_2O_2 Impinger	H_2O_2 content reduced for sites using low sulfur fuel to save reagent and reduce analysis problem	6/77	5.9
NO_x Analysis	Changed to EPA Method 7 because NO_x deteriorates in bag used to take and transport sample for analysis.	8/78	5.3.4 6.4 8.11
As and Sb Analysis	Wet methods deleted, SSMS method of choice.	6/78	8.1
SSMS Analysis	Completely revised to reflect program experience.	9/78	8.3
Slurry Sampling	Procedure modified to reflect EPA Level 1 change. No samples taken by old method	6/78	5.4
Total Chromatographable Organics (TCO)	Dropped for all SASS train samples except XAD-2 resin extract and condensate extract. EPA Level 1 change.	8/78	3.7.1 7.2 7.7 7.8
Liquid Chromatography (LC)	Dropped Fraction 8. EPA Level 1 change.	7/77	7.2 7.8
Liquid Chromatography	Original Level 1 procedure retained when TCO is less than 10% of total organics.	7/77	3.7.1 7.2
XAD-2 Module Condensate	Sample not analyzed if it is less than 10% of the organics in the XAD-2 extract. Only acid extraction performed.	7/77	3.6 7.2
Batch LRMS on LC Fractions	Official EPA change not implemented becasue of cost impact and the procedure was not in original scope of work. Original Level 1 criteria retained.	7/77	3.6 7.2 7.9

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This procedure manual has been prepared for the Industrial and Environmental Research Laboratory, Chemical Processes Branch, Research Triangle Park, North Carolina, as required by EPA Contract 68-02-2197 for Emissions Assessment of Conventional Combustion Systems. Dr. Ron Venezia is the Project Officer at CPB and Mr. Birch Matthews is Program Manager at TRW.

The Chemistry Department of the Chemistry and Chemical Engineering Laboratory, Applied Technology Division was responsible for the work performed on this task.

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D.G. Ackerman
R.B. Beimer
T. Eggleston
B. Eisenberg
A. Grant
M.L. Kraft
D.J. Luciani
R.F. Maddalone
E. Moon
M.O'Rell
S. Reynolds
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1.0 INTRODUCTION

1.1 GENERAL INFORMATION

This procedures manual has been prepared for the Industrial and Environmental Research Laboratory, Chemical Processes Branch, Research Triangle Park, North Carolina, as required by EPA Contract 68-02-2197 for Emissions Assessment of Conventional Combustion Systems. Dr. Ron Venezia is the Project Officer at CPB and Mr. Birch Matthews is Program Manager at TRW.

The objective of this project is to assess air and water pollutants generated by conventional stationary combustion systems including those pollutants generated from related solid waste disposal. The final assessment will be based upon appropriate existing emissions data as well as new data acquired through source sampling and analysis. To accomplish this objective, the project scope of work will include the following activities:

1) Define criteria for determining the adequacy of existing emissions data.
2) Identify emission source categories or category portions which have been adequately assessed based upon the developed criteria.
3) Specify those source categories that require additional investigation.
4) Develop a test program to complete the emissions assessment.
5) Implement the test program and complete the emissions assessment.

The manual describes an integrated set of sampling and analytical procedures for conventional combustion sources which are compatible with the information requirements of a comprehensive Level 1 environmental assessment. The purpose of the data to be generated by these tests is to ultimately provide emission factors for conventional stationary combustion sources.

The procedures are designed to be an integral part of the phased environmental assessment approach and apply primarily to Level 1. The purpose of the initial phase is to obtain preliminary environmental assessment information, identify problem areas and provide the basis for the prioritization of streams, components and classes of materials for further testing by more stringent techniques and procedures. As such, the results of the sampling and of the corresponding analysis procedures are quantitative within a factor of ± 2 to 3. A detailed discussion of the approach along with the criteria used for method selection is given in the IERL-RTP Document # EPA-600/2-76-160a, IERL Procedures Manual: Level 1, Environmental Assessment, which has been the guideline for preparation of this document and by reference, is made an integral part of it.

The manual has been designed to fit the specific sampling and analysis requirements for this program although it is recognized that the procedures are general enough to be modified easily for EPA activities relating to other emission sources. Recognizing that the document is being issued after the initial phase of the program, minor to substantive revisions will be necessary to some procedures as data and experience are gained and as program needs change which would require adapting methods. Thus, it is anticipated that a review and revision process will take place continually during the remainder of the program. Revisions will be documented and controlled in accordance with a standard TRW document control system described in the QA section.

Level 2 sampling and analysis has not been systematically addressed in the manual because it is impossible to predict how the Level 1 results of this program will affect the need for Level 2 analysis. Consequently, Level 2 sampling and analysis plans will be submitted as these requirements are made known. In the case of polynuclear aromatic hydrocarbons (PAH), and sulfur compound determinations, Level 2 needs are presently delineated and consequently procedures are included for sampling and analysis of these materials.

1.2 MULTIMEDIA SAMPLING PROCEDURES

The Level 1 procedure described in this manual can be utilized to acquire process samples, effluent samples, and feed stock samples. The Level 1 environmental assessment program must, at a minimum, acquire a sample from each process feed stock stream, and from each process effluent stream. The feed streams data are necessary to establish a baseline for comparison. The effluent stream sampling program is required to determine the mass emissions rate and the corresponding environmental insult. Consequently, all samples will be taken downstream of any control devices. Sampling and analytical procedures which are required to support comprehensive environmental source assessments must be multimedia in nature.

1.2.1 Classification of Streams for Sampling Purposes

The basic multimedia sampling strategy shown in overview form in Figure 1-1 has been organized around the three general types of samples found in industrial and energy producing processes. This facilitates the complex and difficult tasks of organizing the manpower and equipment necessary for successful field sampling and establishing meaningful units of cost.

The three sample types are:

- Gas/Vapor - These include samples from input and output process streams, process vents, ducts, stacks and ambient air. The samples will be examined for light hydrocarbons and inorganic gases as well as entrained particulates.
- Liquid/Slurry Streams - Liquid streams are defined as those containing less than 5 percent solids. Slurries are defined as those containing greater than 5 percent solids. Non-slowing pastes are considered solids.
- Solids - These include a broad range of material sizes from large lumps to powders and dusts, as well as non-flowing wet pastes.

Flow diagrams which show the overall relationship of the samples to the analysis scheme are shown in Figures 1-2 and 1-3.

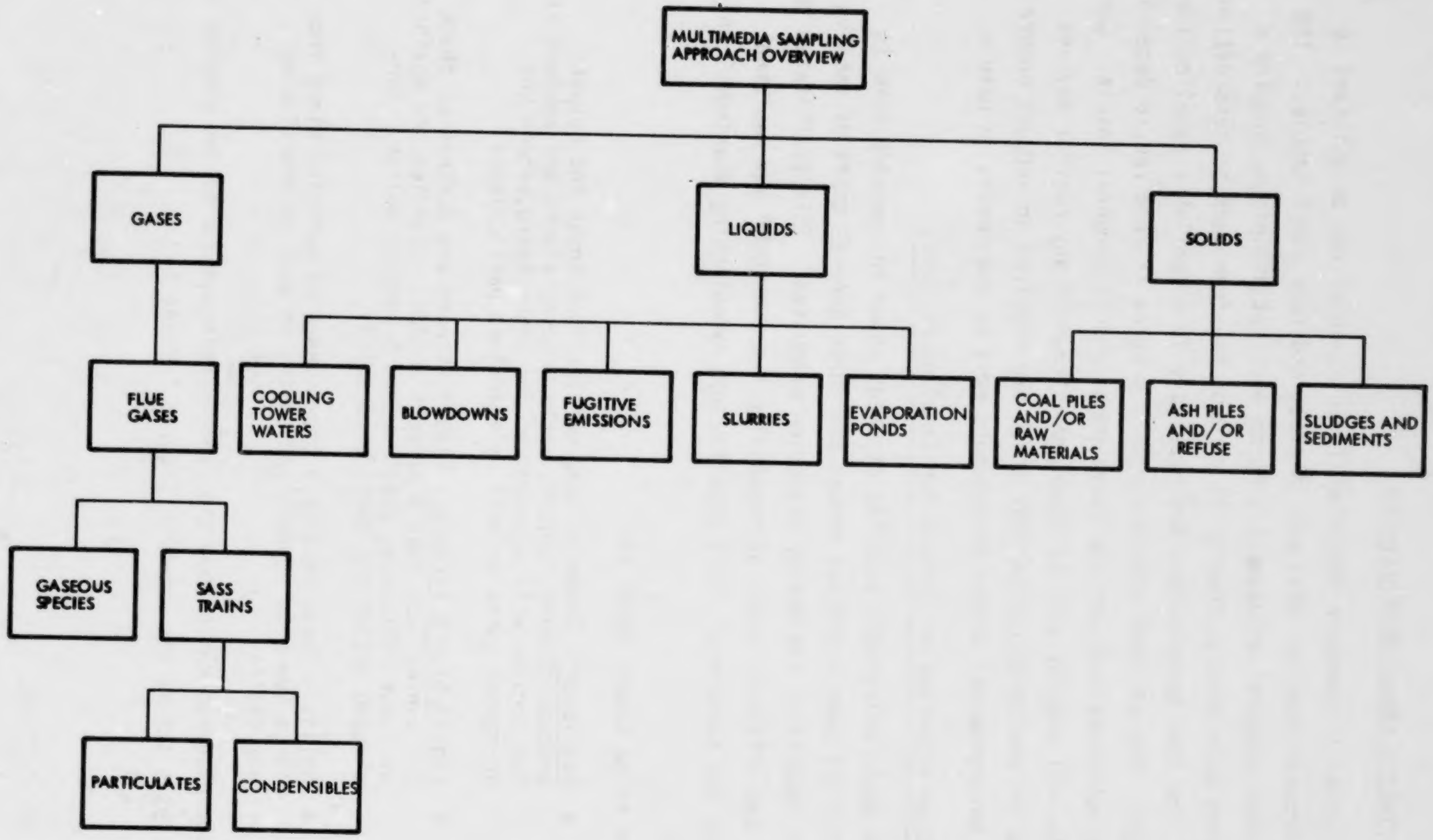

MULTIMEDIA SAMPLING APPROACH OVERVIEW
GASES
LIQUIDS
SOLIDS
FLUE GASES
COOLING TOWER WATERS
BLOWDOWNS
FUGITIVE EMISSIONS
SLURRIES
EVAPORATION PONDS
COAL PILES AND/OR RAW MATERIALS
ASH PILES AND/OR REFUSE
SLUDGES AND SEDIMENTS
GASEOUS SPECIES
SASS TRAINS
PARTICULATES
CONDENSIBLES

Figure 1-1. Multimedia Sampling Approach Overview

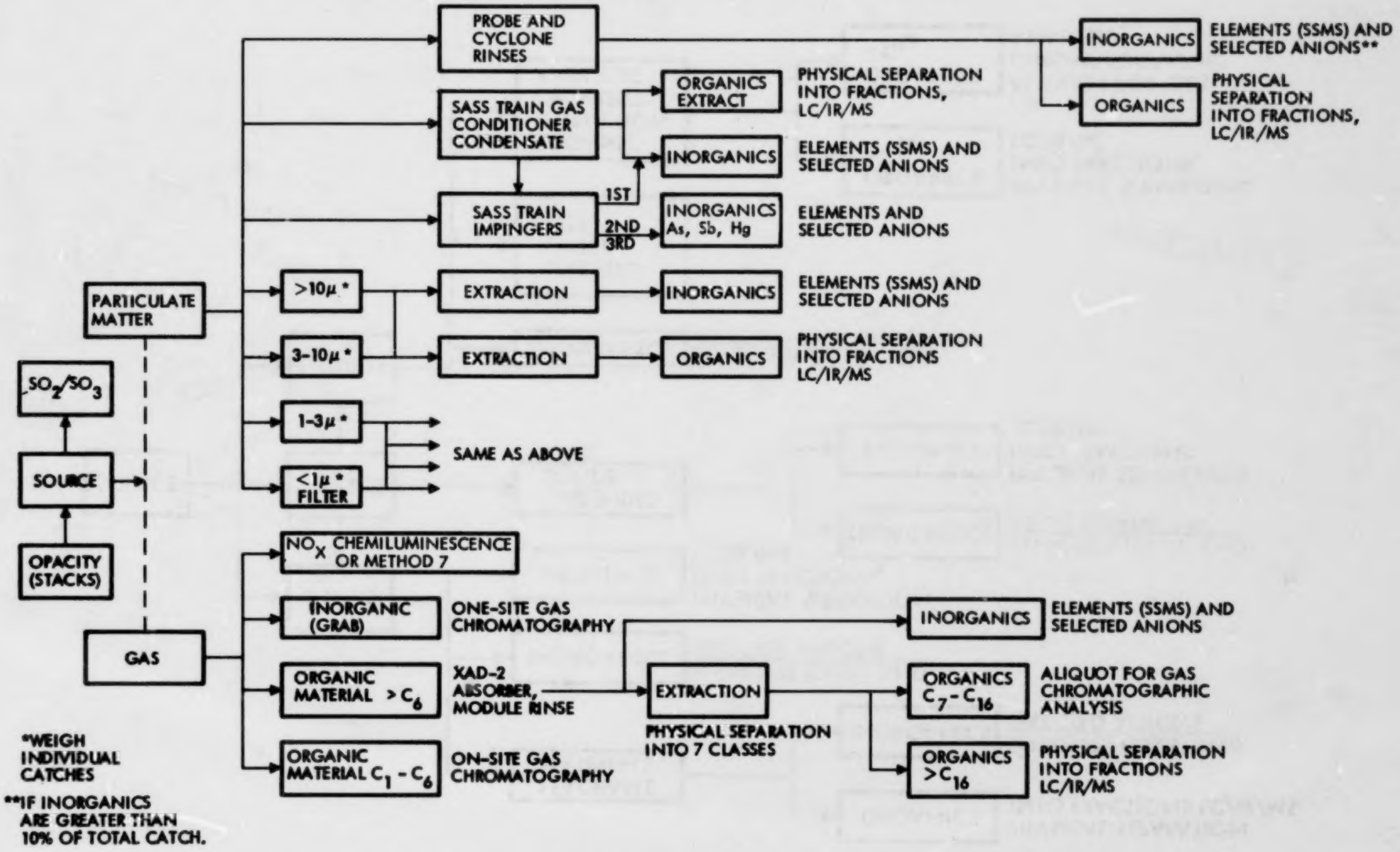

PARTICULATE MATTER
PROBE AND CYCLONE RINSES
INORGANICS
ELEMENTS (SSMS) AND SELECTED ANIONS**
ORGANICS
PHYSICAL SEPARATION INTO FRACTIONS, LC/IR/MS
SASS TRAIN GAS CONDITIONER CONDENSATE
ORGANICS EXTRACT
PHYSICAL SEPARATION INTO FRACTIONS, LC/IR/MS
INORGANICS
ELEMENTS (SSMS) AND SELECTED ANIONS
SASS TRAIN IMPINGERS
1ST
2ND
3RD
INORGANICS As, Sb, Hg
ELEMENTS AND SELECTED ANIONS
>10μ *
3-10μ *
EXTRACTION
INORGANICS
ELEMENTS (SSMS) AND SELECTED ANIONS
EXTRACTION
ORGANICS
PHYSICAL SEPARATION INTO FRACTIONS LC/IR/MS
1-3μ *
<1μ * FILTER
SAME AS ABOVE
SO2/SO3
SOURCE
OPACITY (STACKS)
GAS
NOX CHEMILUMINESCENCE OR METHOD 7
INORGANIC (GRAB)
ONE-SITE GAS CHROMATOGRAPHY
ORGANIC MATERIAL >C6
XAD-2 ABSORBER, MODULE RINSE
EXTRACTION
PHYSICAL SEPARATION INTO 7 CLASSES
INORGANICS
ELEMENTS (SSMS) AND SELECTED ANIONS
ORGANICS C7 - C16
ALIQUOT FOR GAS CHROMATOGRAPHIC ANALYSIS
ORGANICS >C16
PHYSICAL SEPARATION INTO FRACTIONS LC/IR/MS
ORGANIC MATERIAL C1 - C6
ON-SITE GAS CHROMATOGRAPHY
*WEIGH INDIVIDUAL CATCHES
**IF INORGANICS ARE GREATER THAN 10% OF TOTAL CATCH.

Figure 1-2. Basic Level 1 Sampling and Analytical Scheme for Particulates and Gases

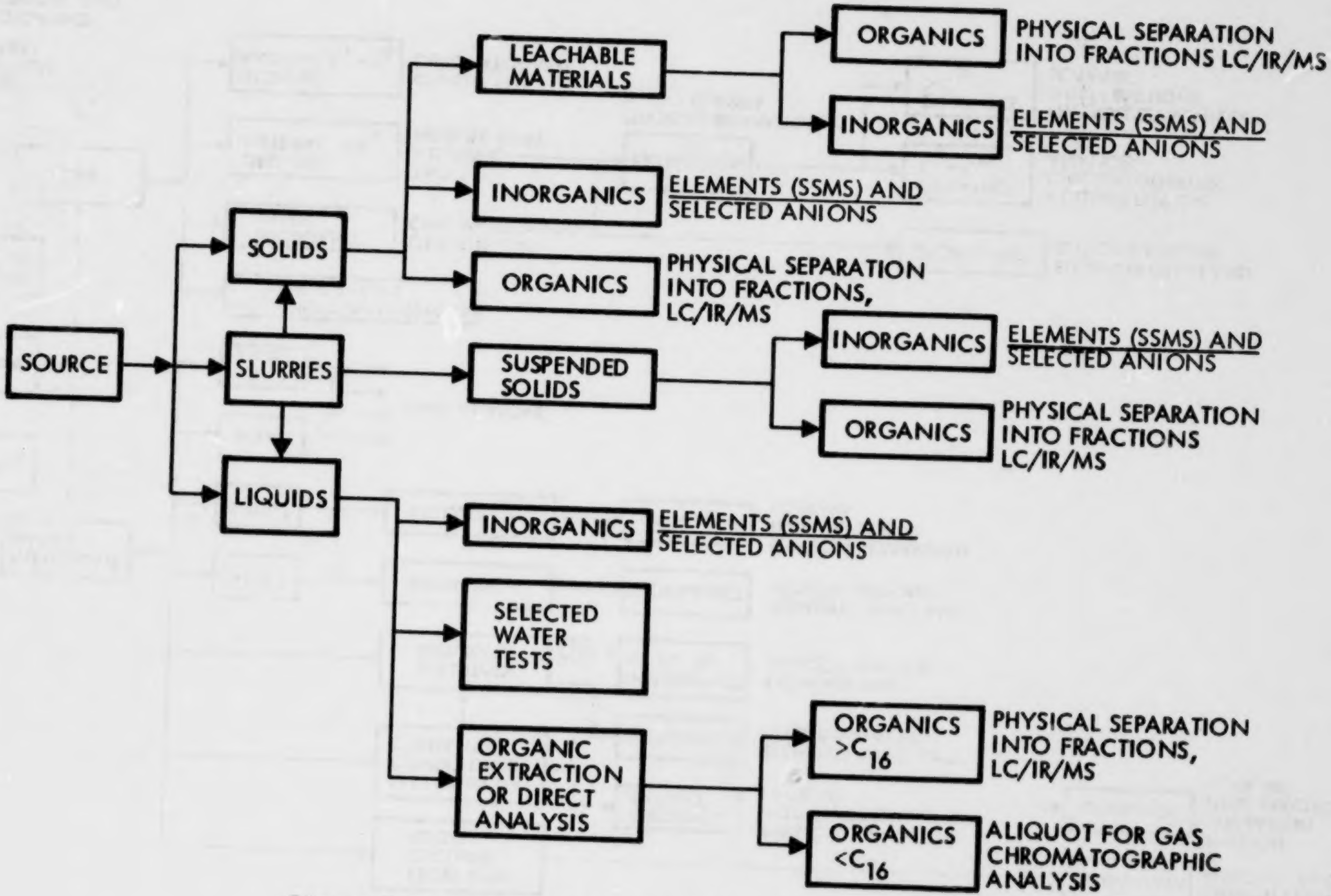

SOURCE
SOLIDS
SLURRIES
LIQUIDS
LEACHABLE MATERIALS
ORGANICS
PHYSICAL SEPARATION INTO FRACTIONS LC/IR/MS
INORGANICS
ELEMENTS (SSMS) AND SELECTED ANIONS
INORGANICS
ELEMENTS (SSMS) AND SELECTED ANIONS
ORGANICS
PHYSICAL SEPARATION INTO FRACTIONS, LC/IR/MS
SUSPENDED SOLIDS
INORGANICS
ELEMENTS (SSMS) AND SELECTED ANIONS
ORGANICS
PHYSICAL SEPARATION INTO FRACTIONS LC/IR/MS
INORGANICS
ELEMENTS (SSMS) AND SELECTED ANIONS
SELECTED WATER TESTS
ORGANIC EXTRACTION OR DIRECT ANALYSIS
ORGANICS >C16
PHYSICAL SEPARATION INTO FRACTIONS, LC/IR/MS
ORGANICS <C16
ALIQUOT FOR GAS CHROMATOGRAPHIC ANALYSIS

Figure 1-3. Basic Level 1 Sampling and Analytical Scheme for Solids, Slurries and Liquids

1.3 ANALYSIS OF SAMPLES

Chapters 6 through 8 specify recommended analysis schemes and procedures that will provide data that can be related both to existing EPA standards and those additional data requirements specified in this chapter for Level 1 environmental assessment. Because quality assurance is an important part of data acquisition, this area is treated separately in Chapter 2. Also, quality control parameters have been integrated into all the procedures. The decision criteria for sampling and analysis is covered in Chapter 3. Chapter 4 describes sample handling and disbursement procedures while Chapter 5 details the acquisition of ducted air and water emissions, liquids, slurries, solids and fugitive air and water emissions, as well as the sample recovery and handling procedures necessary to ready the samples for analysis.

There are five categories of analysis:

- Organic Analysis - Qualitative and quantitative techniques are used to identify compound classes by functional group and boiling point range.
- Inorganic Analysis - Based primarily on spark source mass spectroscopy (SSMS) which can perform a general survey of all effluent streams for possible inorganic elements and atomic absorption spectrophotometry (AAS) for specific elements.
- Water Analysis - Reagent test kits will be used as a supplement for those analyses that are not covered by SSMS or organic analysis.
- Field GC Analysis - Consists of on-site analysis of gaseous and/or low boiling organic and inorganic species.
- Opacity - This test will be performed using a simple Ringelmann Chart and the Bacharach test.

Table 1-1 shows the recommended sample volumes that must be collected in order to obtain the listed sensitivities when the recommended analysis method is used. These sensitivities have been selected by PMB-IERL-RTP for both inorganic and organic compounds so that all species of current interest can be analyzed at levels which at present are the lower limits of environmental concern. Table 1-2 provides a complete list of the analysis procedures, a brief description of the procedures and the section number where each can be found in the manual.

Table 1-1. Recommended Sample Sizes and Detection Limits

Sample Source		Sample Type	Inorganic	Organic
Stack	$30m^3$ $(1,060ft^3)$	Particulate Matter	$0.01\mu g/m^3$	$2\mu g/m^3$
		Sorbent Trap, $>C_{16}$ b)	$0.01\mu g/m^3$	$2\mu g/m^3$
		Sorbent Trap, C_7-C_{16} c)	-	$2\mu g/m^3$
Gas d)	3 liters	General Components	$1 mg/m^3$ e)	$100\mu g/m^3$ f)
		Sulfur Compounds g)	$1\mu g/m^3$	$1\mu g/m^3$
Liquid	∿15 liters (4 gal)	10 ℓ on-site extraction		$10\mu g/l$ h)
		1 ℓ pH <2 with HNO_3	$1\mu g/l$ i)	
		1 ℓ neutral j)		
Solid	1 kg (2.2 lb)	--	1 mg/g	100 ng/g

a) At STP

b) The analysis is terminated for organic material if less than 15 mg ($0.5 mg/m^3$) of organic components are extracted from the total sample.

c) Assumes that the XAD extract is concentrated to 10 ml and a 1 µl sample is injected into a G.C. with a flame ionization detector with a 0.1 ng detection limit.

d) A maximum sample size of 10 ml is assigned for all cases.

e) Detection limit is approximately 1 ppm.

f) Detection limit is approximately 0.1 ppm.

g) Detection limit is approximately 1 ppb.

h) Detection limit of 100 µg/class.

i) Assuming a 1.0 ml sample for SSMS electrode formation and a 10^{-9}g instrument sensitivity.

j) Reserve sample.

Table 1-2. List of Analysis Procedures in the Combustion Source Assessment Methods and Procedures Manual

PARAMETER OF INTEREST	METHOD DESCRIPTION	SECTION NUMBER IN MANUAL
FIELD GAS ANALYSIS		
C_1-C_6 Hydrocarbons	Gas Chromatography	6.2
CO_2, O_2, N_2 and CO	Gas Chromatography	6.2
NO_x	Chemiluminescence or Method 7 (laboratory analysis)	6.3 6.4
FIELD WATER ANALYSES		
Acidity	Titration with NaOH to pH 4 and pH 8	6.5.1
Alkalinity	H_2SO_4 titration to pH 4.5 with two indicators	6.5.2
Conductivity	Self-contained conductivity meter	6.5.3
Total Suspended Solids (TSS)	Spectrophotometry (turbidimetry)	6.5.4
Hardness	Na_2 EDTA titration	6.5.5
pH	Direct reading electrode	6.5.6
Nitrate Nitrogen	Diazotization followed by spectrophotometry	6.5.7
Phosphate, Total Organic and Inorganic	Oxidation with potassium persulfate and spectrophotometry	6.5.8
Sulfite	Iodide-iodate titration	6.5.9
Sulfate	Precipitation with $BaCl_2$ and turbidimetry using SulfaVer IV Test Kit	6.5.10
Cyanide	Colorimetry using Hach Cyanide Test Kit	6.5.11
Ammonia Nitrogen	Nessler (mercuric and potassium iodide)	6.5.12
Opacity	Ringelmann and Bacharach tests	6.6 and 6.7

Table 1-2. List of Analysis Procedures in the Combustion Source Assessment Methods and Procedures Manual (Continued)

PARAMETER OF INTEREST	METHOD DESCRIPTION	SECTION NUMBER IN MANUAL
LABORATORY ANALYSES		
Organic Analyses		
Extraction of samples	Liquid-liquid and Soxhlet solvent extractions	7.3
Concentration	Kuderna-Danish exaporative concentrations	7.4
Gravimetric determinations	Analytical balance weighing of organic residues	7.5
Infrared spectrometry	Salt window smears and KBr pellets	7.6
C_7-C_{16} hydrocarbons	Gas chromatography	7.7
Liquid chromatography	Seven fraction separation on silica gel	7.8
Low resolution mass spectrometry	Solids probe, temperature programmed analysis	7.9
PAHs	Combined gas chromatography/ mass spectrometry	7.10
Inorganic Analyses		
Sample preparation	Parr bomb combustion, Soxhlet aqua regia extraction, hot water digestion	8.2
Spark source mass spectrometry	Graphite electrodes with visual photographic plate data interpretation	8.3
Mercury	$SnCl_2$ reduction and measurement by AAS: cold vapor method	8.4
Arsenic	Hydride generation and AAS detection	8.5
Antimony	Hydride generation and AAS detection	8.6
Sulfate	Turbidimetric measurement of barium sulfate precipitate in suspension	8.7
Sulfur species	Controlled Condensation System (CCS) for determination of SO_2, SO_3 and particulate sulfate	8.8
Fluoride	Selective ion electrode	8.9
Chloride	Selective ion electrode	8.10

2.0 QUALITY ASSURANCE

2.1 PURPOSE

The primary objective of the Quality Assurance function is to ensure that all data collected and reported are meaningful, precise and accurate within the stated acceptance criteria. In designing the Quality Assurance procedure described in this chapter, both the EPA* and TRW quality assurance and guidelines were adapted to the specific requirements of this program. This goal will be accomplished by:

- A continuing evaluation of the adequacy and effectiveness of the overall quality control program,
- Verifying strict adherence to equipment, specification, and procedural requirements
- Requiring correction of weaknesses in the quality program.

2.2 QUALITY POLICIES

The data quality program will verify that the data generated by project personnel meet all the established criteria. The data quality program will have the following characteristics:

- It will be complete in nature. Not only in-house activities, but also the activities of associate contractors and subcontractors will be included. This QA program will cover sampling, analysis, data processing and handling, and all supporting activities in these areas.
- It will be integrated. All procedures will include quality control provisions delineating the practices, requirements and procedures which are to be implemented at each phase of the program.

The quality program will be implemented at two levels:

- Quality control level. To ensure that data quality is sufficient to meet project requirements, all procedures are to be approved by the QA Manager prior to implementation.

---

* Franklin Smith and James Buchanan, "IERL-RTP Data Quality Manual", EPA 600/2-76-159, U.S. Government Printing Office, Washington, D.C. 1976

- Quality assurance level. Quality assurance procedures for independently monitoring and assessing the efficiency and adequacy of individual quality control programs will be administered by the QA office with full power to enforce changes in procedures as needed. Such procedures are subject to periodic review and audit by the EPA Quality Contractor RTI.

The primary objectives of this data quality program are to determine, ensure, and document that the quality (i.e., precision, accuracy, and completeness) of measurements made on this program is commensurate with the end use of the data. Management, administrative, statistical, investigative, preventive, and corrective techniques will be employed for this purpose.

2.3 QUALITY OBJECTIVES

Specific quality objectives for this program are:

- To require that approved procedures are used between various sites and laboratories.
- To review quality among various sites and laboratories and account for disparities to the extent possible.
- To identify the need for and contribute to the selection of procedures and methods necessary to secure the collection of data of acceptable quality (i.e., of acceptable precision, accuracy and completeness).
- To verify that quality control programs are developed for use on each specific sampling and analysis task.
- To develop and implement a quality assurance process which will independently monitor the effectiveness of these individual quality control programs.

2.4 ORGANIZATION

The Quality Assurance Manager will report directly to the Program Manager. He will have complete freedom to inspect, audit, and otherwise review each parameter, process, etc., throughout the program. Quality recommendations will be reviewed and implementation enabled by the Program Office. The QA manager will interface with EPA and other contractors regarding the QA Program to aid in incorporation of optimum controls.

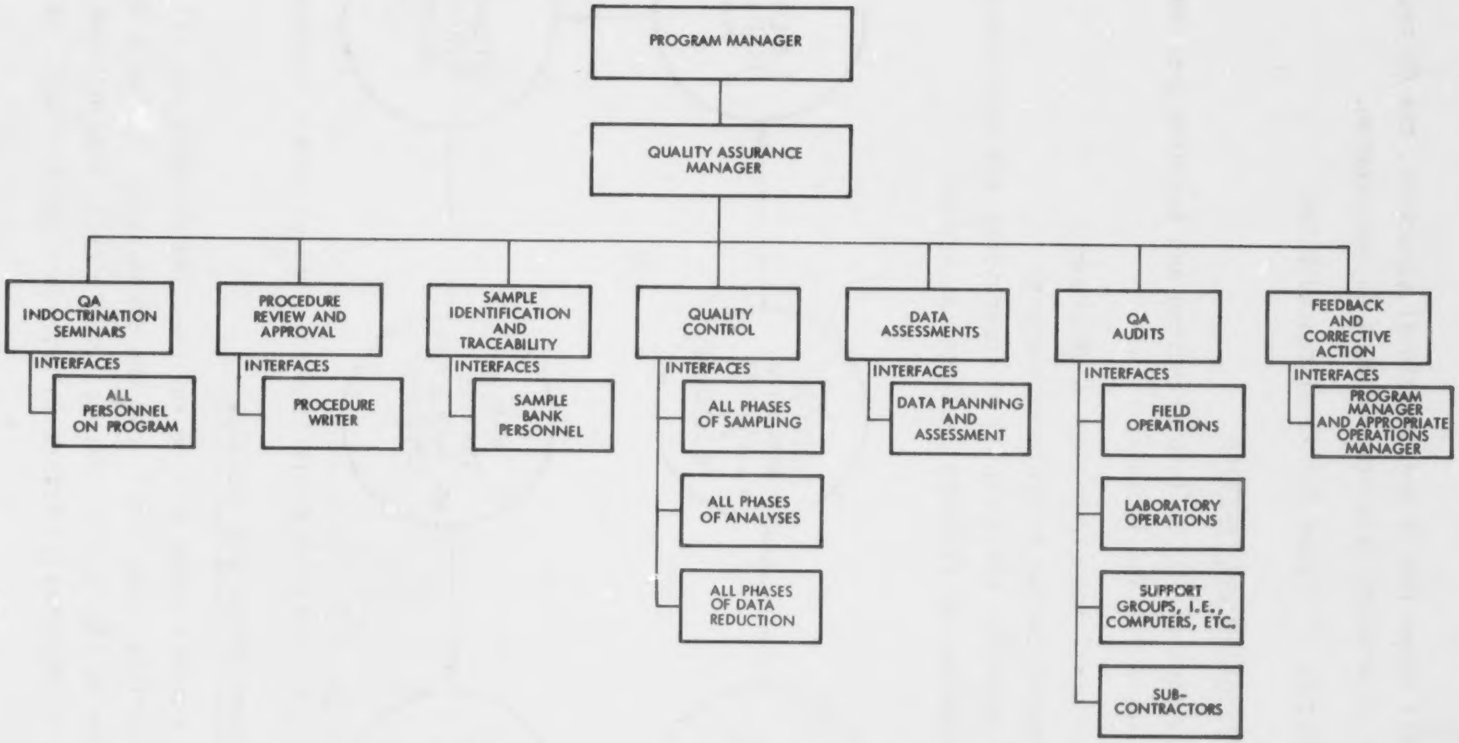

PROGRAM MANAGER
QUALITY ASSURANCE MANAGER
QA INDOCTRINATION SEMINARS
INTERFACES
ALL PERSONNEL ON PROGRAM
PROCEDURE REVIEW AND APPROVAL
INTERFACES
PROCEDURE WRITER
SAMPLE IDENTIFICATION AND TRACEABILITY
INTERFACES
SAMPLE BANK PERSONNEL
QUALITY CONTROL
INTERFACES
ALL PHASES OF SAMPLING
ALL PHASES OF ANALYSES
ALL PHASES OF DATA REDUCTION
DATA ASSESSMENTS
INTERFACES
DATA PLANNING AND ASSESSMENT
QA AUDITS
INTERFACES
FIELD OPERATIONS
LABORATORY OPERATIONS
SUPPORT GROUPS, I.E., COMPUTERS, ETC.
SUB-CONTRACTORS
FEEDBACK AND CORRECTIVE ACTION
INTERFACES
PROGRAM MANAGER AND APPROPRIATE OPERATIONS MANAGER

Figure 2-1. Function Diagram for Quality Assurance

2.5 QA TASKS

Figure 2-1 shows the QA organizational structure, the QA tasks, and the required interfacing with other groups on the program.

Each category of Figure 2-1 is discussed below.

2.5.1 Indoctrination and Training

The activities of the QA indoctrination and training program are outlined in Figure 2-2 and include:

- Personnel indoctrination to QA program
- Identification of training elements
- Preparation and training of supervisory and test personnel
- Refresher QC training meetings, as needed

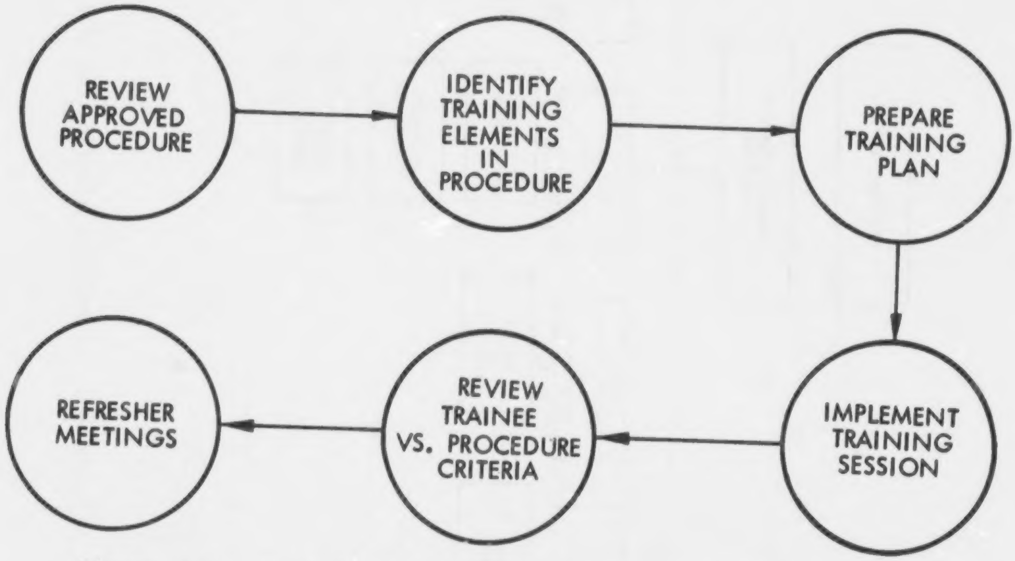
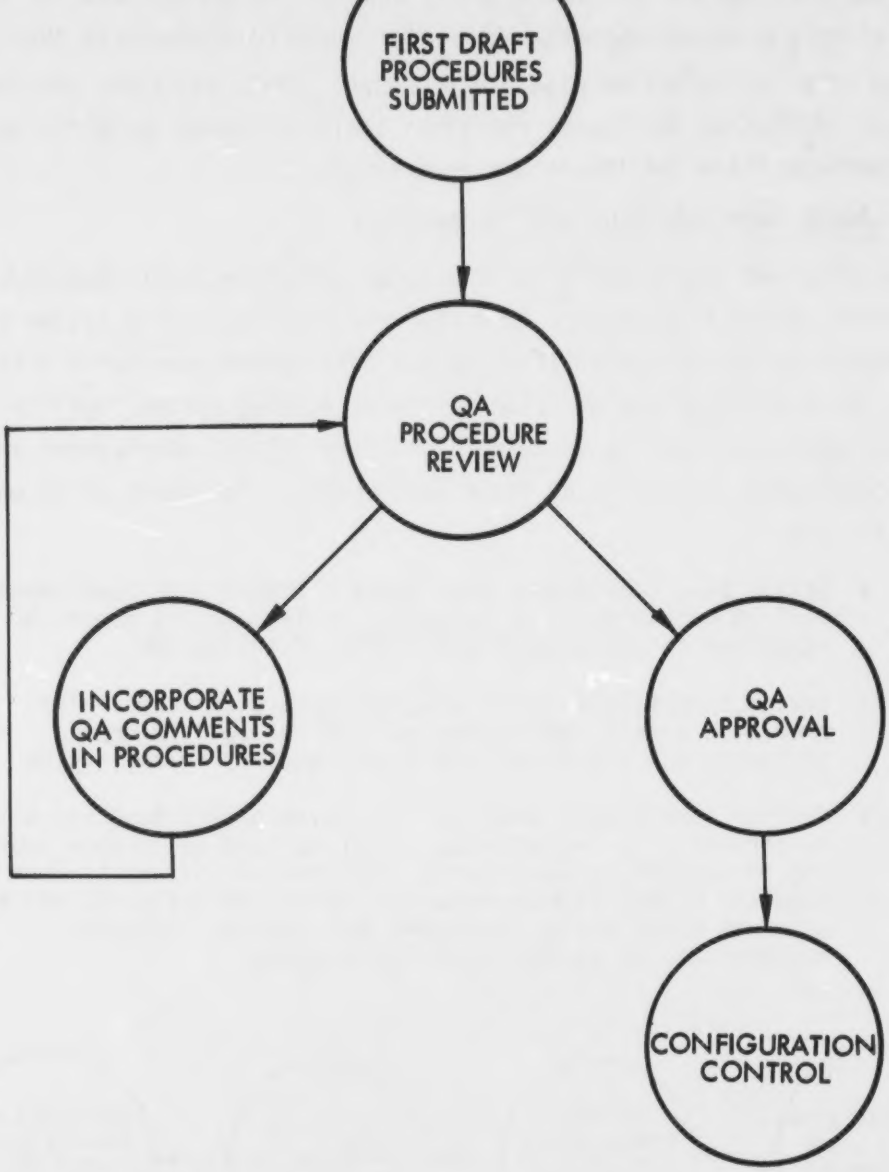

REVIEW APPROVED PROCEDURE
IDENTIFY TRAINING ELEMENTS IN PROCEDURE
PREPARE TRAINING PLAN
IMPLEMENT TRAINING SESSION
REVIEW TRAINEE VS. PROCEDURE CRITERIA
REFRESHER MEETINGS

Figure 2-2. Training Activity Associated with Each Procedure

2.5.2 Procedure Review and Approval

Quality control steps will be reviewed and approved for all procedures, instructions, specifications, equipment, etc. The QA approval cycle is shown in Figure 2-3. Because of the cycle time between QA and the authors, a concentrated effort in procedure approval will be necessary.



FIRST DRAFT PROCEDURES SUBMITTED
QA PROCEDURE REVIEW
INCORPORATE QA COMMENTS IN PROCEDURES
QA APPROVAL
CONFIGURATION CONTROL

Figure 2-3. QA Function Relative to Procedures

QA will also ensure that the documentation system will maintain a current configuration (latest revision) of procedures being used in testing. There is a requirement that whenever it is evident that data being obtained are not sufficiently accurate or appropriate for the intent of this program, the sampling and/or analytical procedure shall be modified after coordination with other groups. Thus, revisions are to be expected. A list of the latest revisions shall be issued by QA for posting by appropriate field and laboratory supervisors.

2.5.3 Sample Identification and Traceability

The size and complexity of this program, which includes thousands of data points coming from several laboratories, requires a firm system of data processing and accountability. Since this system provides a vital link in the quality of the emission source assessment system, Quality Assurance personnel will contribute in both its initial development and in the continuous monitoring of its effectiveness. The tasks as shown in Figure 2-4 are:

- Sample Bank Development Assistance - Sample bank development will be monitored by QA to assist in introducing proper QC steps and to increase dependability of the system.

- Review Sample Bank System and Implementation Forms - The completed sample bank system will be reviewed in detail, including all procedures and forms required in the system.

- Monitor Sample Bank Function - The sample bank function will be periodically inspected to ensure up-to-date, proper labeling of samples, proper control and traceability maintained on samples, proper disbursement of samples for analyses, and that all data books are accompanying each sample. Complete traceability of samples shall be verified.

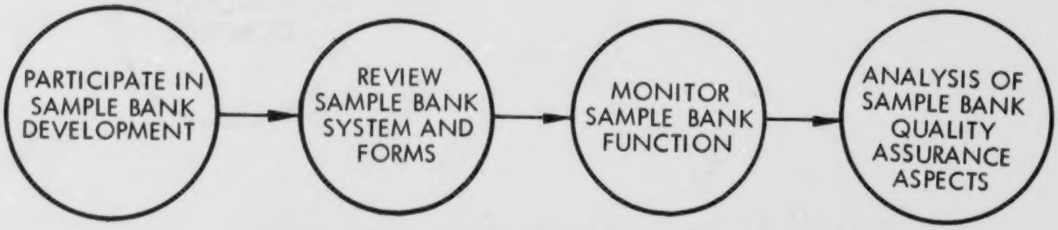

PARTICIPATE IN SAMPLE BANK DEVELOPMENT
REVIEW SAMPLE BANK SYSTEM AND FORMS
MONITOR SAMPLE BANK FUNCTION
ANALYSIS OF SAMPLE BANK QUALITY ASSURANCE ASPECTS

Figure 2-4. QA Activities for the Sample Bank

- Analysis and Reports of Sample Bank - An assessment of the sample bank system will be made, including traceability, based on the results of this inspection. Criteria for this assessment will be based on the requirement that the sample bank should be able to show the exact treatment sequence and the dates of the various critical types of treatment (i.e., stabilization, digestion and titration, etc.) for each sample.

2.5.4 Quality Control

The following key aspects of the QA effort in this program for reviewing the adequacy of the QC Program are shown in Figure 2-5 and discussed below.

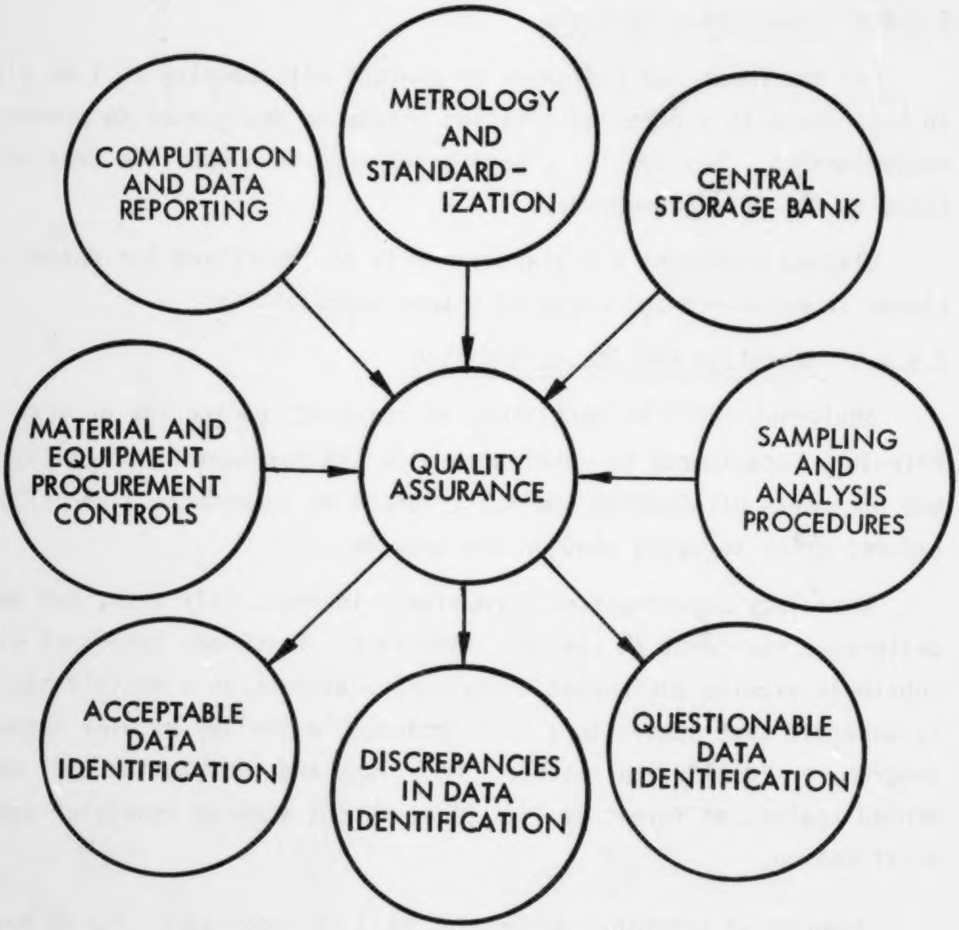

COMPUTATION AND DATA REPORTING
METROLOGY AND STANDARDIZATION
CENTRAL STORAGE BANK
MATERIAL AND EQUIPMENT PROCUREMENT CONTROLS
QUALITY ASSURANCE
SAMPLING AND ANALYSIS PROCEDURES
ACCEPTABLE DATA IDENTIFICATION
DISCREPANCIES IN DATA IDENTIFICATION
QUESTIONABLE DATA IDENTIFICATION

Figure 2-5. Quality Control Operations to be Emphasized in this Program

2.5.4.1 Procurement Quality Control

- All procured materials must conform to the appropriate procedure specification.
- Reagents and chemicals that have limited shelf life will be identified and used within the specified expiration date.
- All acceptance tested materials and equipment procured for this program will be inventoried. Traceability of all acceptance testing, including all data and test methods, will be maintained. Discrepant procurement, fabrication, cleanliness, metrology, standardization, materials and processes, etc., will be subjected to discrepancy analysis (see Section 2.5.7).

2.5.4.2 Cleanliness Controls

All equipment and glassware in contact with samples will be cleaned in accordance to a detailed cleaning procedure designated to prevent contamination. Any special cleaning required in a specific test will be added to the test procedure.

Cleaned equipment and glassware will be identified and dated, or stored in dated storage areas to ensure traceability.

2.5.4.3 Metrology and Standardization

Equipment shall be certified, as required, by the TRW or GCA Metrology Departments in accordance with EPA Document 600/2-76-159 or DOD Documents MIL-Q-9858A and MIL-C-45662A or acceptable alternative procedures prior to being used on the program.

Metrology Department will routinely inspect, calibrate, and certify designated equipment at specific intervals. Metrology personnel will routinely examine designated analytical equipment on a monthly basis. It is expected that contractors will implement a similar regular inspection program, or justify its absence. Metrology and calibration will be documented against an inventory list of equipment showing scheduled equipment verification.

Results of metrology activities will be reported to the QA Manager of this program.

2.5.4.4 Central Storage Bank Quality Control

The data bank and sample identification system for this program (see Chapter 4) will include controls on the overall quality of the system. Some of the QC factors to be considered in these controls are:

- Legibility.
- Permanence of record.
- Standardization of notation.
- Completeness check list at each significant data transfer step.
- Systematic storage of in-process data forms, sample location, etc.

2.5.5 Computation and Data Reporting

The QA functions in the data assessment area are shown in Figure 2-6 and consist of the following:

- Verification of the acceptability of the computation steps and calculation checks used in the analytical procedures. This will include any computer programs for processing raw data.
- Statistical evaluation of comparisons between standards, replicates, spiked samples and the routine analyses.
- Records and trend analyses to identify potential QA problem areas in the assessment scheme.
- Data validation procedures shall be defined for all measurement systems.
- Provision for clear definition of various parameters, such as flow rates and calibration data.
- Use of minimum detectable limits to evaluate trace data for appropriateness.
- Examination of negative data points immediately for possible cause, error, interferences.
- Concern with all rejected data and the cause or reason for rejection.
- Relation between data and standards, replicates, spikes, etc., and Level 1 requirements.

2.5.6 Auditing

Quality audits will be made of all the critical functions in the emission study program. The audits will include:

- Verification that standards, procedures, records, drawings, specifications, requirements, etc., are maintained in the most current approved version.
- Verification that actual practice in tests, data storage, sampling, etc., agrees with approved written instructions.

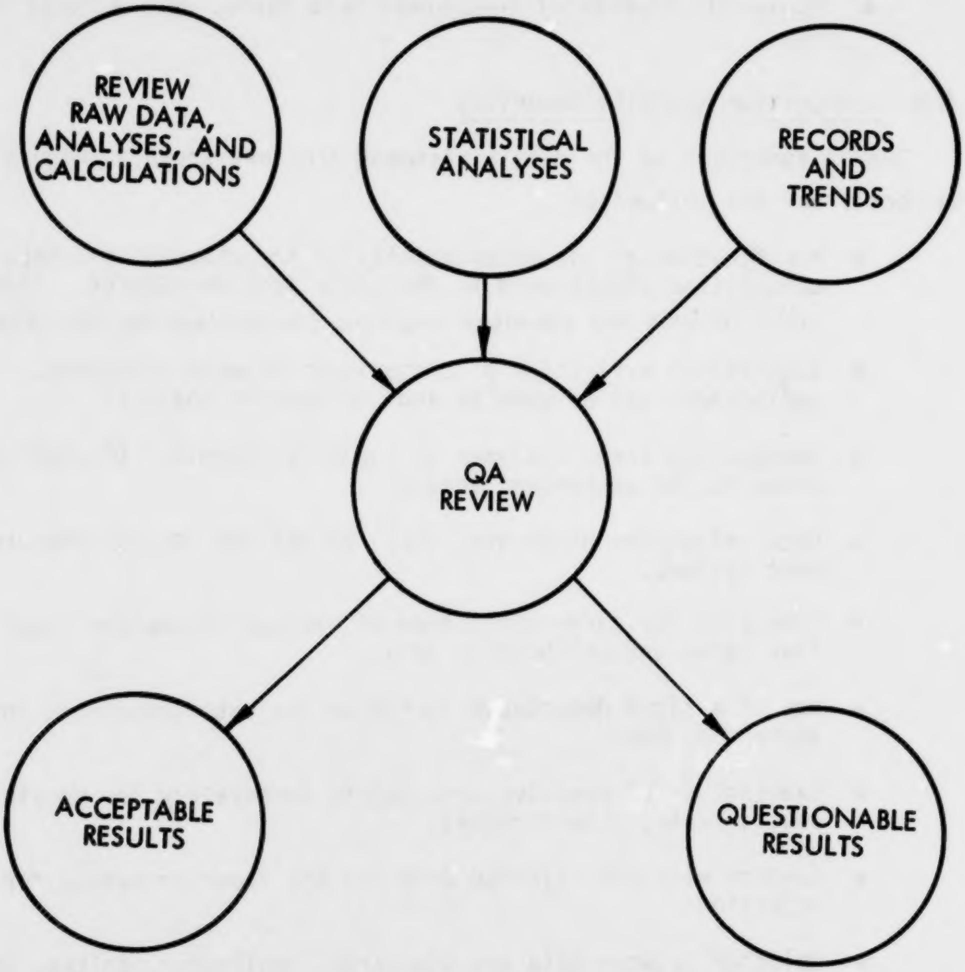

REVIEW RAW DATA, ANALYSES, AND CALCULATIONS
STATISTICAL ANALYSES
RECORDS AND TRENDS
QA REVIEW
ACCEPTABLE RESULTS
QUESTIONABLE RESULTS

Figure 2-6. Activities in the Quality Data Validation and Assessment Program

- Assessment of adequate Quality Control of program by use of replicate samples, independent analyses, spiked samples, "dry runs," traceability studies, etc.

- Providing substantiative evidence that failure risk is controlled by the use of precautionary measures, such as cleanliness, orderliness, environmental control, and by the use of industry-accepted techniques for common technical operations.

Auditing will be done as shown in Figure 2-7, by apportioning a percentage of the total auditing effort to: (a) purely random selection of audit material; (b) a percentage to areas either totally new or suspected to be "weak links" in the quality control system; (c) and the remaining to areas which are found to be "trouble spots" due to high frequency of repair, schedule delay, replacements, spoilage, or poor performance in the most recent audit.

2.5.6.1 Audit Items

A review will be made of all functions required for this program through existing documentation such as processing flow diagrams, data flow diagrams, procedures, procurement practices, etc. Two kinds of audits will be performed: quantitative and qualitative. The quantitative audit will utilize check methods such as standard analytical samples, and spiked samples. The qualitative audit will assess and document (1) facilities; (2) equipment; (3) systems; (4) record keeping; (5) data validation; (6) operation, maintenance, and calibration procedures; and (7) reporting aspects of the total quality control program.

2.5.6.2 Audit Apportionment

Audit apportioning will consist of allocation of audit effort among random audits, suspect item audits and problem audits within the constraints of the program. The auditing effort may be qualitative, quantitative, or both, and either a complete audit or a partial audit may be allocated.

2.5.6.3 Audit Frequency and Schedule

Auditing frequency will be determined by the nature of the audit effort, its cost, risk factors in not auditing, and priority.

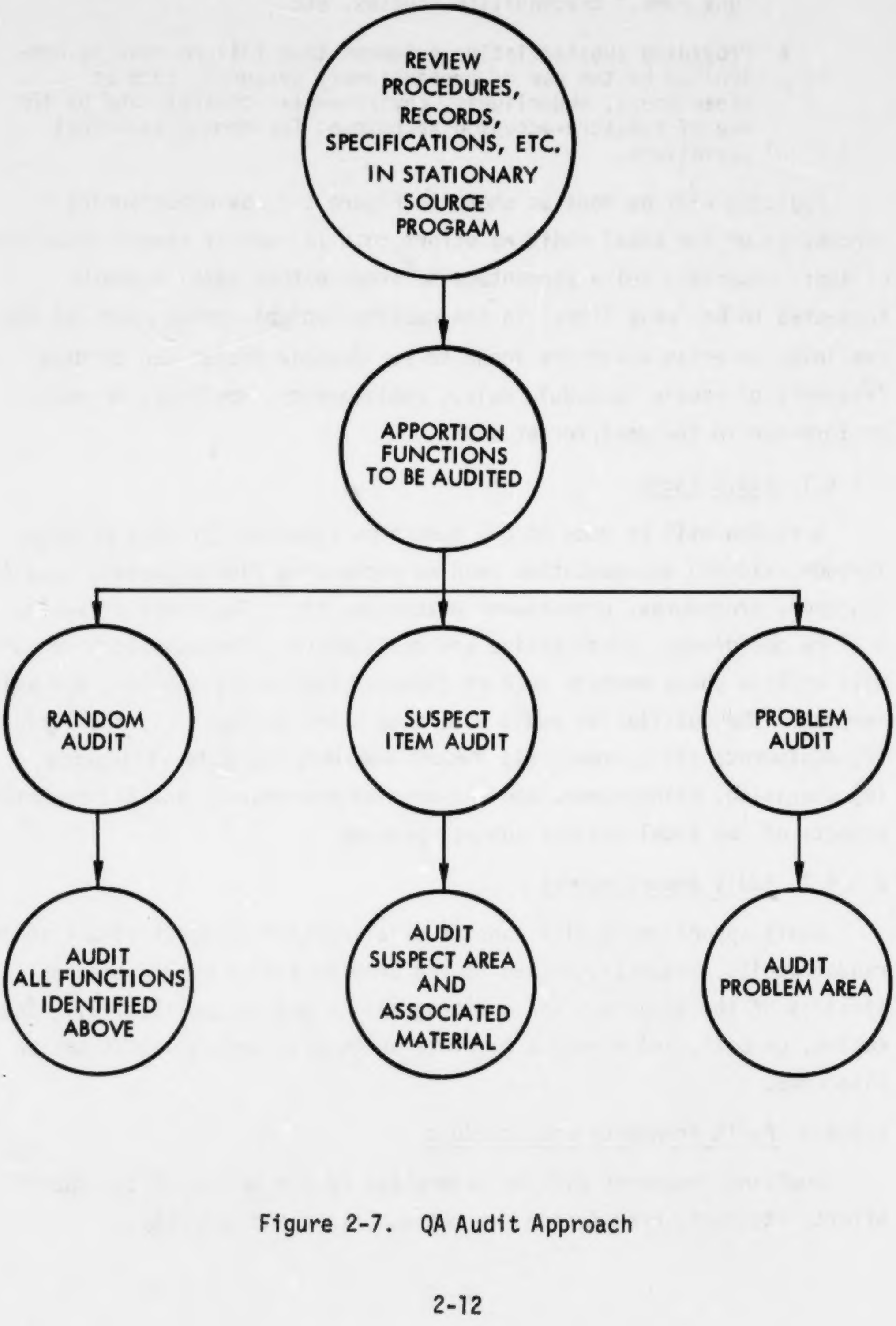

REVIEW PROCEDURES, RECORDS, SPECIFICATIONS, ETC. IN STATIONARY SOURCE PROGRAM
APPORTION FUNCTIONS TO BE AUDITED
RANDOM AUDIT
SUSPECT ITEM AUDIT
PROBLEM AUDIT
AUDIT ALL FUNCTIONS IDENTIFIED ABOVE
AUDIT SUSPECT AREA AND ASSOCIATED MATERIAL
AUDIT PROBLEM AREA

Figure 2-7. QA Audit Approach

Functions in which problems have been identified will generally be of highest priority. Areas suspected of being "weak links" in the data chain, for example, a process having marginal reproducibility characteristics, will be of next concern. Of lowest priority, yet of importance, is the random auditing of any process to sample for continued process acceptability. For this program, random audits will be held on at least two sites during the first year. Using constraints of schedule, cost, and availability of the audit function, random audits must be considered along with the problem and suspect area audits. To do this, an integrated approach will be used in which audit activities are combined in an audit visit as much as possible. Excessive problem demand or similar demands requiring unplanned QA audit effort will necessarily affect the audit frequency or planning.

2.5.6.4 Audit Procedures

Some general considerations in the audit procedures are:

- Audits will be conducted on all phases of each test via a random selection process without prior notice. Thus, true representative audits will be attained.
- Audits will be conducted in the field, in the laboratory, in the data handling center and in the data assessment areas.
- Subcontractors will also be audited.
- All violations or infractions will be noted and immediate notification of appropriate personnel at all levels will be made. Corrective action must be immediately implemented or the testing will be labeled "Potentially Erroneous Data."
- All unreliable data will be noted and replacement samples or analysis will be performed wherever possible.
- All auditing will consist of observations and notation as to whether approved procedures are used and as to the level of proficiency. Any deviation will immediately be noted.
- When subcontractors are employed to perform certain analytical tasks, a program is established whereby known reference samples are sent to them interspersed with actual samples. The quality of the subcontracting laboratory's work can then be readily determined. Their methods and QA functions are also fully examined so that TRW will have confidence in their data.

- Quality audits shall be coordinated with Data Assessment groups in terms of notification of results. No advance warning will be given to personnel of any impending QA audit in order to assure a valid and representative audit.

2.5.6.5 Audit Performance and Reports

The actual audit and the reporting of the audit findings will be thoroughly documented.

2.5.7 Discrepancies

The efficient and thorough identification of discrepancies in the methodology of emission assessment is essential to maintain effective quality assurance. A discrepancy, for purposes of QA,is considered to be any deviation from accepted procedures, requirements, or processes, or defects in a material part or result compared to a requirement. Discrepancies may arise from QA audits, from any of the quality functions in the program, as well as from other program sources such as procurement, testing, sampling, data handling, etc. Systematic and thorough treatment of discrepancies will follow the plan shown in Figure 2-8. This systematic approach provides a basis for maintaining the quality audit at a minimum sampling level.

The three major activities in which QA must participate are:

- Discrepancy review board participation
- Review of failure analysis and recommendations
- Approval of final closeout activities of problems and discrepancies

2.5.8 Quality Assurance Reporting and Documentation

Quality Assurance will issue special reports of audits in field and/or audits in laboratory. When indications that quality may be compromised exist, depending on the severity of the infraction, meetings of all appropriate personnel would also be instituted.

The final or annual reports will include a section on Quality Assurance. A summarization of all data quality can be given as it relates to:

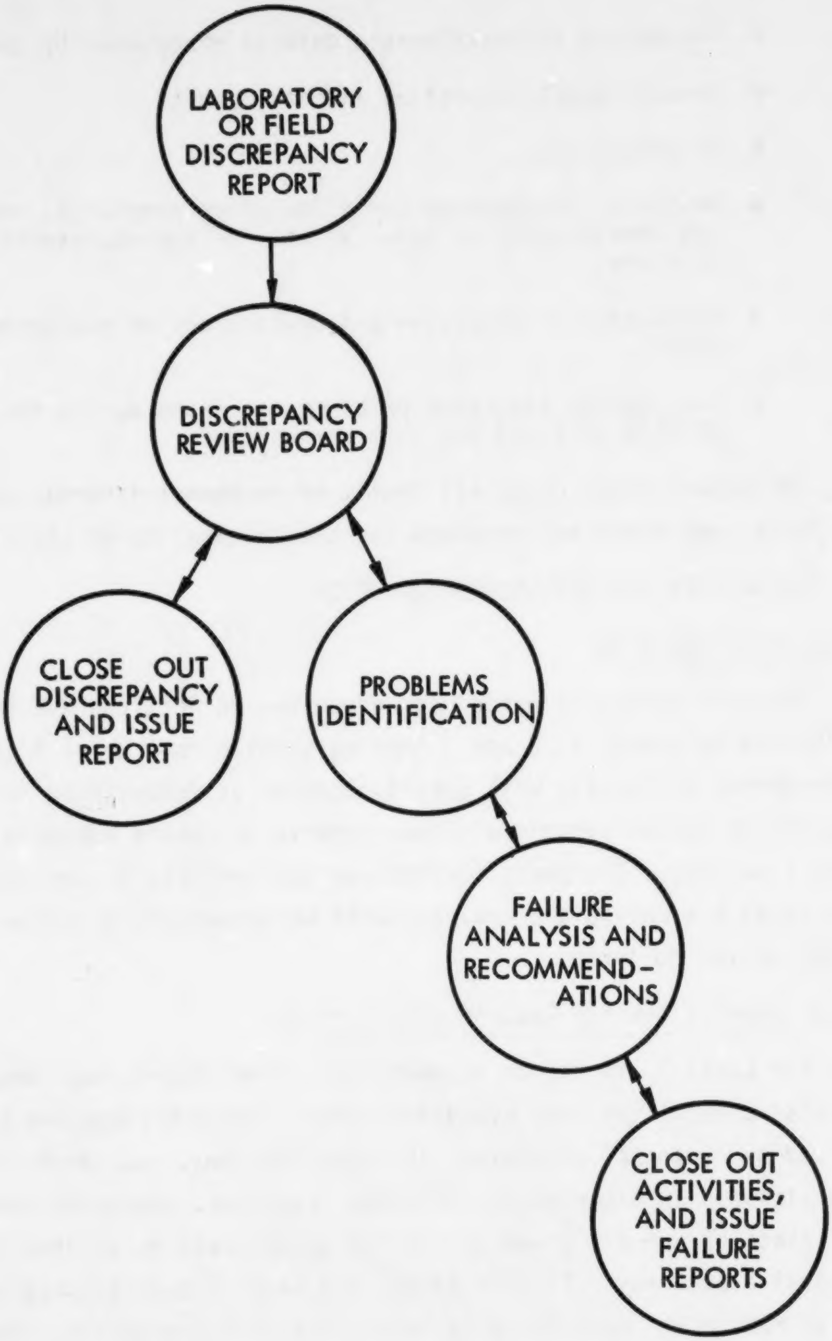

LABORATORY OR FIELD DISCREPANCY REPORT
DISCREPANCY REVIEW BOARD
CLOSE OUT DISCREPANCY AND ISSUE REPORT
PROBLEMS IDENTIFICATION
FAILURE ANALYSIS AND RECOMMEND-ATIONS
CLOSE OUT ACTIVITIES, AND ISSUE FAILURE REPORTS

Figure 2-8. Activities Relative to Discrepancies

- Quality and percentage of replicate samples and replicate analysis.
- Percentage of questionable data as discovered by audits.
- On-site audit inspection and its results.
- Discrepancies.
- Review of performance audit including precision, accuracy, and completeness of data, as well as how representative the data are.
- Discussion of precision and/or accuracy of subcontractors data.
- Any quality assurance problems occurring during the performance of this task and how they were solved.

The report shall go to all levels of personnel in order that they may fully comprehend any problems and the criticality of strict QA/QC.

2.6 GUIDELINES FOR IMPLEMENTATION OF QA

2.6.1 Applicability

The principles and procedures discussed in Sections 2.2 thru 2.5 are applicable to Levels 1, 2 and 3 testing. While many Level 1 tests will be performed optionally with quality control at intensified levels, it is possible to define certain minimum criteria to insure adequate quality for Level 1 testing. The basis for the minimum criteria is the recognition that Level 1 sampling and analyses will be acceptable within an accuracy factor of two to three.

2.6.2 Level 1 Quality Assurance Activities

For Level 1, it can be assumed that normal day-to-day sampling, material control testing, standardization, and metrology are adequately controlled by personnel selection, training programs, equipment controls and supervision. In other words, existing practices, equipment and personnel are "state-of-the-art", and controlled by adequate guidelines and procedures to Level 1 accuracy. If this is so, the Level 1 quality program should aim to reduce the occurrence of excursions from procedures. Excursions would cause gross undetected variation, while procedures, as expected from development work, are adequate to produce Level 1 accuracy.

To do this, the quality program must identify and emphasize the sources of error which are most likely to cause extreme variation. Examples of such gross sources of error are:

- contamination
- cumulative buildup in sampling equipment
- sample loss or concentration
- transposed data numerals
- erroneously marked sample identity
- incorrect physical units or loss of digit in recorded parameter.

In addition, particular procedures may have specific key process steps which, if violated, could cause serious errors where Level 1 accuracy is required. It is therefore assumed that Level 1 accuracy will most probably be exceeded by human error in following actual procedural steps. A method for auditing procedural adherence can be developed by observing procedural adherence a given number of times. One method is described in detail in Appendix A, Section A.

2.6.3 Minimum Number of "Blank" Tests Acceptable for Level 1 Tests

A minimum number of reagent "blank" tests from a container can be found which will indicate further testing is not needed to indicate good quality control practices are being used. The technique can be applied to any procedure in the program which requires blank testing, and will indicate that emission factors are not unduly influenced by unexpected variability among the blanks.

The approach is as follows:

- Identify the desired accuracy requirement for the procedure.
- Estimate the parameter mean, the average change between blanks and its standard deviation obtained from repeated testing of the container for its "blank" value.
- Determine the level of risk to be afforded in assuming blank testing may be stopped.
- Determine the number of tests to show the parameter will not exceed the accuracy requirement with the selected risk of being incorrect, using Equation (A.7) of Appendix A.

More testing is automatically required when the emission values are nearer the detection limit, when the variability is higher, or when a low risk is desired. The procedure is discussed in detail in Appendix A, Section B. It is found, for example, that the repeated testing of "blank" solvent samples could be terminated when 1/4 of the solvent container has been used while maintaining Level 1 accuracy, if the unaccounted variation of the blanks is not more than about ± 0.6% of the emission value. This work indicates that in the Level 1 testing, when the blank is not higher than 10% of the observed value, and is relatively reproducible, repeated testing of the solvent is relatively unproductive. A possible quality assurance test of this assumption can be made by subsequently running a blank on the last of the container to verify the correctness.

2.6.4 Minimum Number of Replicate Tests for Level 1

The decision criteria in this section will determine the minimum extent of analytical test replication needed to support the concept of Level 1 accuracy in the data base. The approach is based on the observation that repeated replication of data after the test has demonstrated an adequate accuracy is useful mainly as a form of insurance against outliers and sudden changes in the reproducibility. For Level 1 accuracy requirements, the need for this insurance is less than with ordinary analytical testing, and an adequate control is provided by strict adherence to procedural details and a QA monitoring program. Thus, the use of replicate testing can be curtailed as soon as it has been demonstrated either that the method is sufficiently accurate for Level 1 purposes, or that the method is not as accurate as desired but further testing adds little to its characterization.

The decision criteria do not apply to replications required because of a suspected error in handling or testing which may occur in a given test. These replications are part of a problem-solving process and are generally not applicable as estimates of normal operation.

Further, if the decision criteria have been applied and replication of a test has ceased, replication should be reinitiated whenever the assumption of test method stability is suspect. For example, if new technicians are introduced, procedures modified or equipment changed, replication should be applied until the decision criteria have evaluated the new conditions.

The decision to cease replication is based simply on having obtained an adequate representation of the variability of the test method. Knowledge of the variability (obtained through replicate analysis) is adequate when there is little risk (less than 10%) that the Level 1 acceptability of the results will be proven wrong by further testing, or for methods having unavoidably high inaccuracy, that further testing will reveal an inaccuracy grossly larger than suspected. In this latter case, "grossly larger" is taken to mean that the method reproducibility estimate itself is within Level 1 accuracy. The development of the approach is given in Appendix A, Section C.

The decision criteria are based on several assumptions:

(1) The reproducibility of the test is not affected by the type of site sampled.

(2) The reproducibility of the test will not change during the course of the program, given one set of procedures and personnel.

(3) The inaccuracy of a pollutant determination is predominately due to random sampling and test variation, i.e., bias, if present, is either relatively small or known and therefore correctable.

(4) The Level 1 accuracy factor for sampling and analysis for each site is 3, and for analysis alone, is 2.

Assumptions (1) and (2) can be checked by quality assurance testing during the program.

2.6.5 Decision Plan for Number of Replicate Tests

The following decision plan, shown schematically in Figure 2-9, defines the actions to be taken to identify the need for replication.

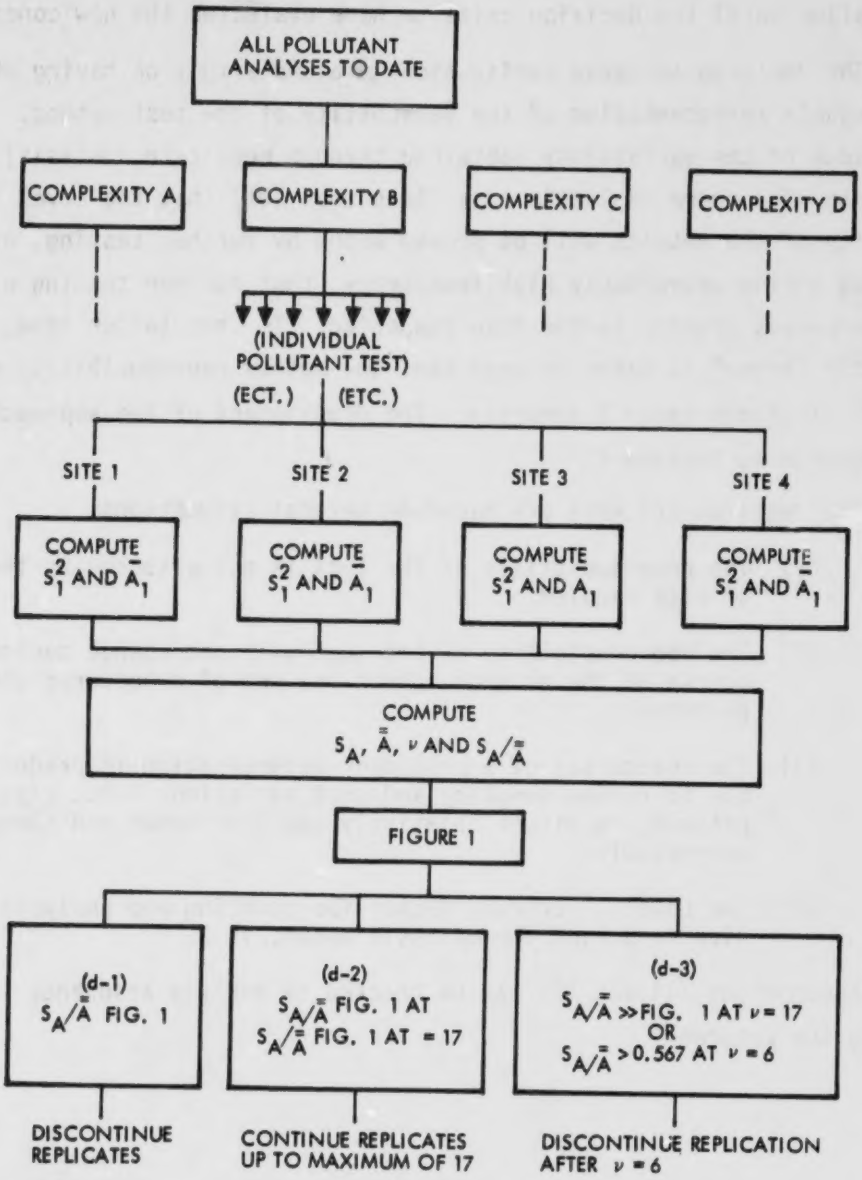

ALL POLLUTANT ANALYSES TO DATE
COMPLEXITY A
COMPLEXITY B
COMPLEXITY C
COMPLEXITY D
(INDIVIDUAL POLLUTANT TEST)
(ECT.)
(ETC.)
SITE 1
SITE 2
SITE 3
SITE 4
COMPUTE S_1^2 AND $\bar{A}_1$
COMPUTE S_1^2 AND $\bar{A}_1$
COMPUTE S_1^2 AND $\bar{A}_1$
COMPUTE S_1^2 AND $\bar{A}_1$
COMPUTE S_A, $\bar{\bar{A}}$, ν AND $S_A/\bar{\bar{A}}$
FIGURE 1
(d-1) $S_A/\bar{\bar{A}}$ FIG. 1
(d-2) $S_{A/\bar{A}}$ = FIG. 1 AT $S_{A/\bar{A}}$ = FIG. 1 AT = 17
(d-3) $S_{A/\bar{A}} \gg$ FIG. 1 AT $\nu = 17$ OR $S_{A/\bar{A}} > 0.567$ AT $\nu = 6$
DISCONTINUE REPLICATES
CONTINUE REPLICATES UP TO MAXIMUM OF 17
DISCONTINUE REPLICATION AFTER $\nu = 6$

Figure 2-9. Decision plan describes the action needed to identify the need for replication

In this plan:

$$s_A = \sqrt{\frac{(n_1-1)\ s_1^2 + (n_2-1)\ s_2^2 + \ldots\ (n_\nu-1)\ s_\nu^2}{n_1 + n_1 + \ldots n_\nu - \nu}}$$

where each s^2 is the variance of the test results for the pollutant at a given site, and each n is the number of tests for that pollutant at that site.

$\bar{A}$ is computed as the average value of the pollutant determination of each of the four complexities shown in Figure 3-2. Compute $\bar{A}$ as:

$$\bar{A} = \frac{n_1\bar{A}_1 + n_2\bar{A}_2 + \ldots n_\nu\bar{A}_\nu}{n_1 + n_2 + \ldots n_\nu}$$

where $\bar{A}$, etc., are the individual site average values.

If only duplicates are taken at each site,

$$\bar{A} = \frac{\bar{A}_1 + \bar{A}_2 + \ldots \bar{A}_\nu}{\nu}$$

$$\nu = (n_1 - 1) + n_2 - 1 + \ldots (n_\nu - 1)$$

where n_1 is the number of repeated tests for pollutant A at site 1 of the complexity group.

For Application of the Criteria

d-1 Discontinue replicate testing when the value of $S_A/\bar{\bar{A}}$ at the level of ν used is less than that required by Figure 2-10.

d-2 When $S_A/\bar{\bar{A}}$ is greater than that required by Figure 2-10 at the level of ν used, but less than the curve at $\nu = 17$, (i.e., 0.310), continue testing until d-1 is met or 17 replicates have accrued ($\nu = 17$).

d-3 When $S_A/\bar{\bar{A}}$ will clearly not meet the criterion at $\nu = 17$ (i.e., the value of $S_A/\bar{\bar{A}}$ is sufficiently larger than the curve criterion, that it is highly unlikely that added testing will improve S_A or $\bar{\bar{A}}$ sufficiently to meet the criterion), stop replication at $\nu = 6$.

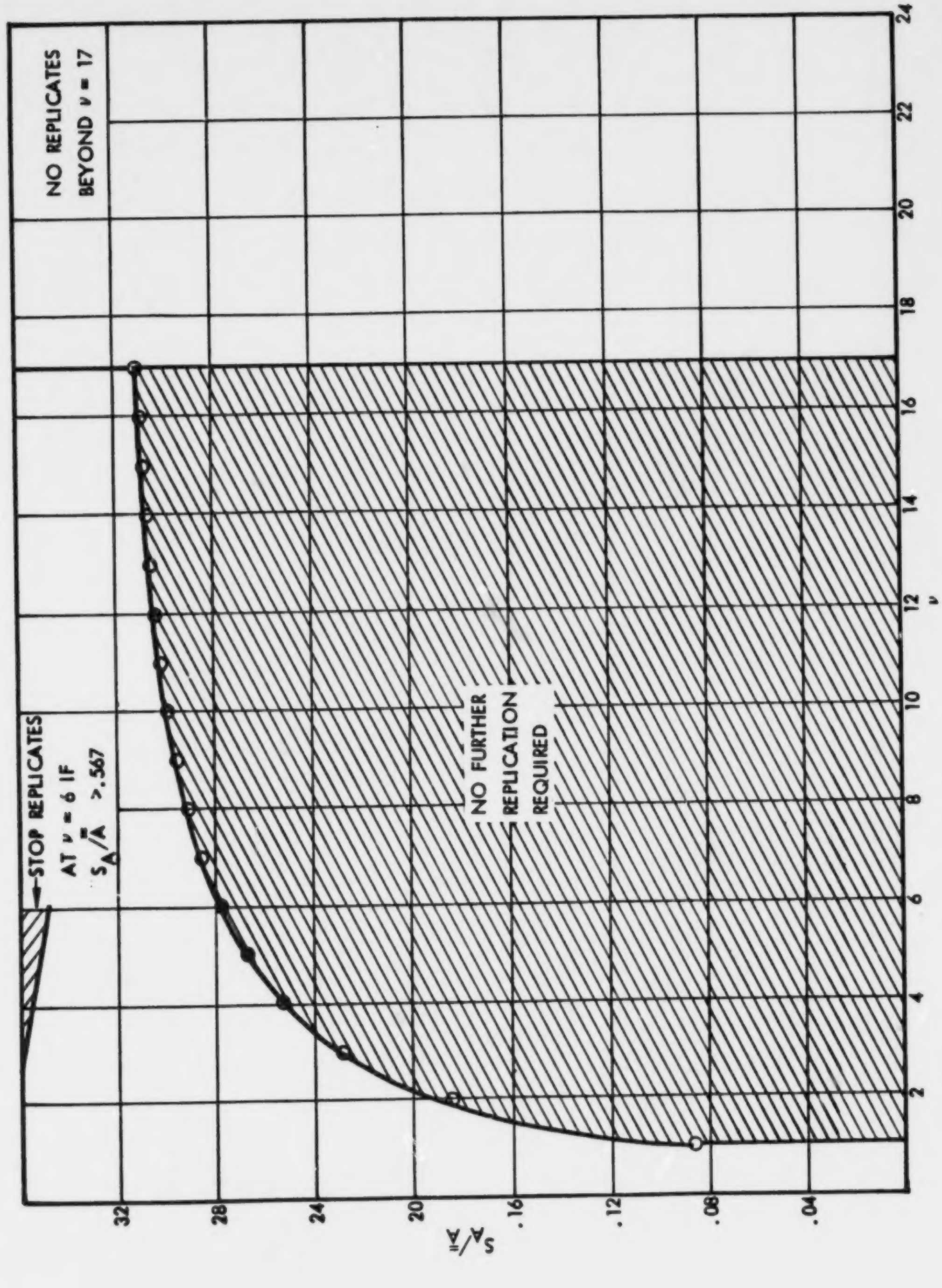


Figure 2-10. Decision Criterion for Replication of Laboratory Tests

3.0 SAMPLING AND ANALYSIS DECISION CRITERIA

3.1 INTRODUCTION

This chapter presents the basic decision and planning criteria that will be used in the design and execution of the entire sampling and analysis program. These decision criteria also outline the approach for acquiring special samples and/or data not normally collected for a Level 1 environmental assessment. A set of criteria are given for cases in which either sample availability or data availability may limit the number of analyses that may be performed. Samples such as fuel, water, ash, and slurries are available in large quantities and will not require analytical prioritization. Samples from the SASS train will often require a prioritization matrix in order to make effective use of the available sample. Because planning and analysis decisions concerning the analysis of SASS train samples for organics can not be made solely on the basis of sample weight, a nomograph has been developed to predict the amount of extractable organics and allow decisions to be made concerning those cases which warrant solvent extraction and a full range of organic analysis. In addition, an approach to effluent water sampling and analysis is presented.

3.2 REQUIREMENTS OF PLANNING AND ASSESSMENT TASK

As part of every environmental assessment, a planning and assessment (P&A) task is necessary to give overall focus to the sampling and analysis tasks. The initial work for this program will center on the review and evaluation of the existing emissions inventory as it relates to the combustion sources identified for study. This assessment and prioritization effort will be part of the early phases of the program. This will result in the generation of an overall field testing and laboratory analysis plan designed to acquire additional emissions data for those sources and emissions species which are determined to be presently inadequate. Because the data to be generated by the analysis task is based on the assumption that no prior data exist, the actual needs of data for assessment purposes will override all subsequent decision criteria.

Planning and assessment activities continue throughout this project to evaluate the data from the sampling and analysis effort and from other sources as it becomes available. In other words, an iterative process will continue in the area of emissions assessment, source prioritization, field sampling, and laboratory analysis as new data are generated or become available and as the project emphasis shifts.

3.3 FIELD SAMPLING AND ANALYSIS DECISION CRITERIA

A set of guidelines must be developed for the field sampling crews in order to 1) gather samples for analysis in a cost-effective manner, 2) meet the requirements of the planning and assessment task, and 3) meet the needs of laboratory operations to generate the proper data. The basic input will be provided by the P&A effort which will define the number of sites and general samples to be taken. This selection process has been treated in other program documents. However, as described in this section, an additional set of criteria has been developed so that the field samples will be taken in a manner that will result in meaningful laboratory analyses. These are described in the following sections, and detailed application of these concepts is given in Chapters 5 and 6.

3.3.1 SASS Train Cyclone Deletion Guidelines

The combustion sources that will be sampled for this program include a significant number of categories burning fuels such as distillate oil, diesel fuel, natural gas, and to a certain extent residual oil that will result in grain loadings below 0.1 grains/SCF. The resulting catches are less than 7 g. As the grain loading is lowered, the >3μ catch in particular drops off rapidly to the point where the 3 and 10μ cyclone catches are too small to be recovered. As the grain loadings are lowered further, the 1μ cyclone catch also approaches zero. The use of cyclones where very small (<10 mg) catches occur will result in high sample loss and contamination. In addition, large amounts of labor are expended precleaning, leak checking and post-cleaning the cyclones in order to obtain nonexistent or very small samples that will result in no useful data being generated. Therefore, for both technical and economic reasons, a set of decision criteria has been developed for removal of the cyclones at lower grain loadings so that a maximum amount of useful data will be generated.

The basis for these criteria is the nomograph shown in Figure 3-1 which displays the estimated >3μ and <3μ catches as a function of grain loading. The data used for this nomograph were obtained from real case sampling efforts using the SASS train[1,2] and comprehensive studies by GCA[3] and MRI[4]. These studies include coal, oil, and gas fired units under a wide range of grain loadings. Because the >3μ fraction drops off to zero as the grain loading goes down and because this is the primary trend that affects the decision criteria displayed below, these data were always interpreted with a conservative positive bias for the weight of the >3μ fraction. This was especially true when two different types of boilers or fuels gave differing particulate distributions. This nomograph has been verified by results obtained on this program.

Based on Figure 3-1, the set of decision criteria for cyclone use shown in Table 3-1 was developed. In general, a projected catch of 5-10 mg in a given cyclone results in that cyclone being eliminated. This cut-off point was chosen because samples of this size represent the lower limit of recovery and are marginal in terms of analysis (only SSMS can be performed). Table 3-2 shows how the decision criteria are expected to apply to the combustion source categories to be tested in this program. In all cases, the conservative approach will be taken, and an additional cyclone will be used for the first one or two sites tested using each type of fuel. In general, these guidelines were found to be adequate. However, in order to make the data output of this program more nearly compatible with the EPA's fine particulate data base, it was agreed that after 1 September 1979 the 3μ cyclone would always be used. In this way, an absolute statement can be made that no particulate greater than 3μ was collected. The revised guidelines are shown in Figures 3-3 and 3-4.

Tables 3-1 and 3-3 are used subject to the following criteria:

- The maximum expected grain loading will be determined using previous test data or estimates provided by site personnel, actual TRW/GCA field experience, and existing data concerning similar sites. When in doubt, the next higher grain loading will be used.

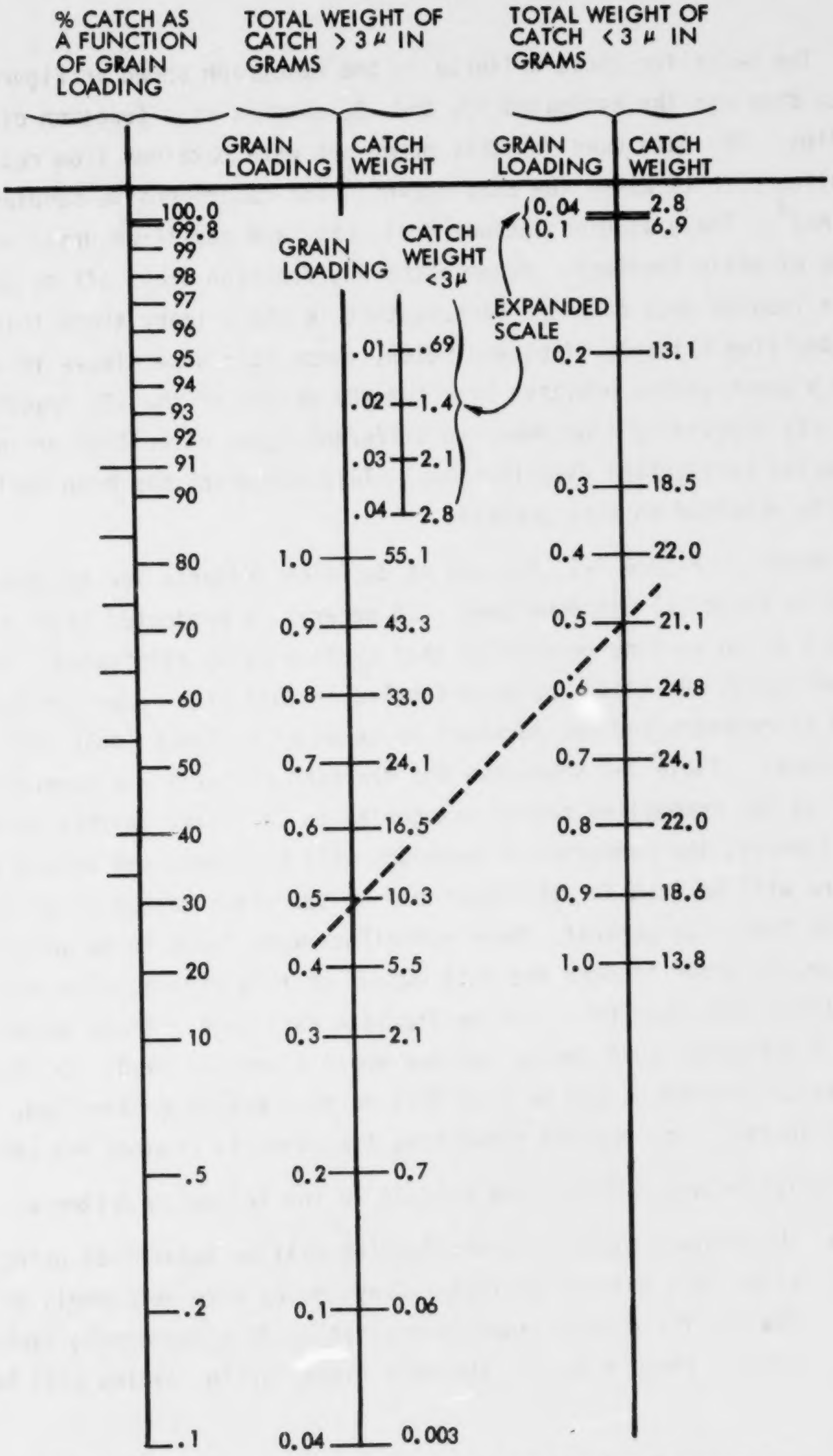


Figure 3-1. Particulate Analysis Prediction Nomograph

Table 3-1. SASS Train Cyclone Use Criteria*
(Before 1 September 1979)

Grain Loading	Projected Catch(g)		Cyclones Required		
	>3μ	<3μ	1μ	3μ	10μ
>0.11	>0.006	>6.9	Yes	Yes	Yes
0.051-0.10	0.004-0.006	3.1-6.9	Yes	Yes	No
0.021-0.050	nil	1.4-3.1	Yes	No	No
0.0001-0.020	nil	0.007-1.4	No	No	No
<0.0001	nil	<.007	Use filter, XAD-2 module and impingers only		

*A filter is used in all cases.

Table 3-2. Expected Application of SASS Train Cyclone Use Criteria as a Function of Fuel Type*
(Before 1 September 1979)

Fuel Type	Projected Grain Loading	Cyclones Required		
		1μ	3μ	10μ
Coal	>0.1	Yes	Yes	Yes
Residual Oil	0.051-0.10	Yes	Yes	No
	0.021-0.05	Yes	No†	No
	<0.020	No	No†	No
Distillate Oil	<0.02	No	No†	No
Diesel Fuel	<0.02	No†	No	No

*A filter is to be used in all cases.

†This cyclone will be used until field tests show that it is not necessary.

Table 3-3. SASS Train Cyclone Use Criteria*
(After 1 September 1979)

Grain Loading	Projected Catch(g)		Cyclones Required		
	>3μ	<3μ	1μ	3μ	10μ
>0.11	>0.006	>6.9	Yes	Yes	Yes
0.051-0.10	0.004-0.006	3.1-6.9	Yes	Yes	No
0.021-0.050	nil	1.4-3.1	No	Yes	No
0.0001-0.020	nil	0.007-1.4	No	Yes	No
<0.0001	nil	<.007	Use filter, XAD-2 module and impingers only		

*A filter is used in all cases.

Table 3-4. Expected Application of SASS Train Cyclone Use Criteria as a Function of Fuel Type*
(After 1 September 1979)

Fuel Type	Projected Grain Loading	Cyclones Required		
		1μ	3μ	10μ
Coal	>0.1	Yes	Yes	Yes
Residual Oil	0.051-0.10	Yes	Yes	No
	0.021-0.05	Yes	Yes	No
	<0.020	No	Yes	No
Distillate Oil	<0.02	No	Yes	No
Diesel Fuel	<0.02	No†	Yes	No

*A filter is to be used in all cases.

†This cyclone will be used until field tests show that it is not necessary.

- All catches will be photomicrographed, checked for significant oversize particulate, and a rough particle size distribution will be determined.
- If the field test produces results that indicate the use of additional cyclones, the test will be repeated.
- If special conditions indicate their need, additional cyclones will be used.

3.3.2 Special Procedures for Home Heating Units

In the case of the home heating units which are not run continuously, the units will be run continuously until the required 30 m^3 (STP) is collected. However, concern over the variation of organic emissions as a function of duty cycles resulted in additional testing of these units with a 20 min. on, 10 min. off and 50 min. on, 10 min. off duty cycles. For both oil and gas fired units, no significant differences were found.

3.3.3 SO_3/SO_2 Measurements

It is the objective of this program to determine SO_3/SO_2 ratios for a selection of large utility combustion sources. These measurements have been the subject of investigation on TRW's EPA Contract 68-02-2165 in which it was found that the most effective method of making these measurements is by a modified Goksoyr-Ross technique as delineated by EPA Document "Guidelines for Combustion Source Sulfuric Acid Emission Measurements." This technique will be used on at least 10 category C and D (Fig. 3-2) sites as stipulated by the Planning and Assessment Task.

3.4 SPECIAL CASE ANALYSIS PLAN

In order to gather data in a cost-effective manner for species of current environmental interest and requiring specialized techniques for sampling and/or analysis and also for samples where considerable data is available, a "Special Case Analysis Plan" has been developed and the major components are shown in Figure 3-3. This plan is designed to show the rationale that will be developed in detail during the program in order to analyze a statistically significant cross-section of samples that will satisfy the needs of the program. The following sections briefly explain the criteria in Figure 3-3. Complexity categories, discussed below, are defined in Figure 3-2.

COMPLEXITY	ASSUMPTIONS FOR GENERALIZED COMPLEXITY CATEGORIES
A GASEOUS EMISSIONS ONLY - GAS AND OIL FIRED COMBUSTION SOURCES	• ALL OIL OR GAS INTERNAL OR EXTERNAL COMBUSTION SOURCES IN THE RESIDENTIAL AND COMMERCIAL/INSTITUTIONAL CLASSES • ALL OIL OR GAS INTERNAL COMBUSTION SOURCES IN THE INDUSTRIAL OR ELECTRICAL GENERATION CLASSES ASSUMPTIONS: 1. NO SIGNIFICANT PARTICULATE >3μ WILL BE COLLECTED 2. NO SIGNIFICANT FUGITIVE EMISSIONS ARE PRESENT 3. NO SOLID STREAMS ARE PRESENT 4. NO WATER STREAMS ARE PRESENT
B GASEOUS/ASH EMISSIONS ONLY - COAL FIRED COMBUSTION SOURCES	• ALL COAL-FIRED COMBUSTION SOURCES IN THE RESIDENTIAL AND COMMERCIAL/INSTITUTIONAL CLASSES ASSUMPTIONS: 1. FULL RANGE OF PARTICULATE WILL BE COLLECTED 2. NO SIGNIFICANT FUGITIVE EMISSIONS ARE PRESENT 3. NO WATER STREAMS ARE PRESENT
C COMPLEX OIL AND GAS FIRED COMBUSTION SOURCES	• ALL EXTERNAL OIL AND GAS FIRED COMBUSTION SOURCES IN INDUSTRIAL AND ELECTRICAL GENERATION CLASSES ASSUMPTIONS: 1. NO SIGNIFICANT PARTICULATE >3μ WILL BE COLLECTED 2. NO SIGNIFICANT FUGITIVE EMISSIONS ARE PRESENT FUGITIVE SURVEY WILL BE PERFORMED AT OIL FIRED SITES IF OBVIOUS PROBLEMS EXIST 3. NO BOTTOM ASH SAMPLES WILL BE TAKEN 4. THREE WATER STREAMS WILL ALL BE SINGLE PHASE
D COMPLEX COAL AND REFUSE FIRED COMBUSTION SOURCES	• ALL COAL AND REFUSE FIRED COMBUSTION SOURCES IN INDUSTRIAL AND ELECTRICAL GENERATION CLASSES ASSUMPTIONS: 1. FULL RANGE OF PARTICULATE WILL BE COLLECTED 2. FUGITIVE EMISSIONS SURVEY WILL BE PERFORMED IF OBVIOUS PROBLEMS EXIST 3. SEVEN WATER STREAMS INCLUDING THREE TWO PHASE STREAMS WILL BE SAMPLED 4. TWO ASH STREAMS INCLUDING BOTTOM ASH AND PARTICULATE CLEAN-UP ASH WILL BE SAMPLED

Figure 3-2. Source Type and Complexity Classification for Level 1 Sampling and Analysis

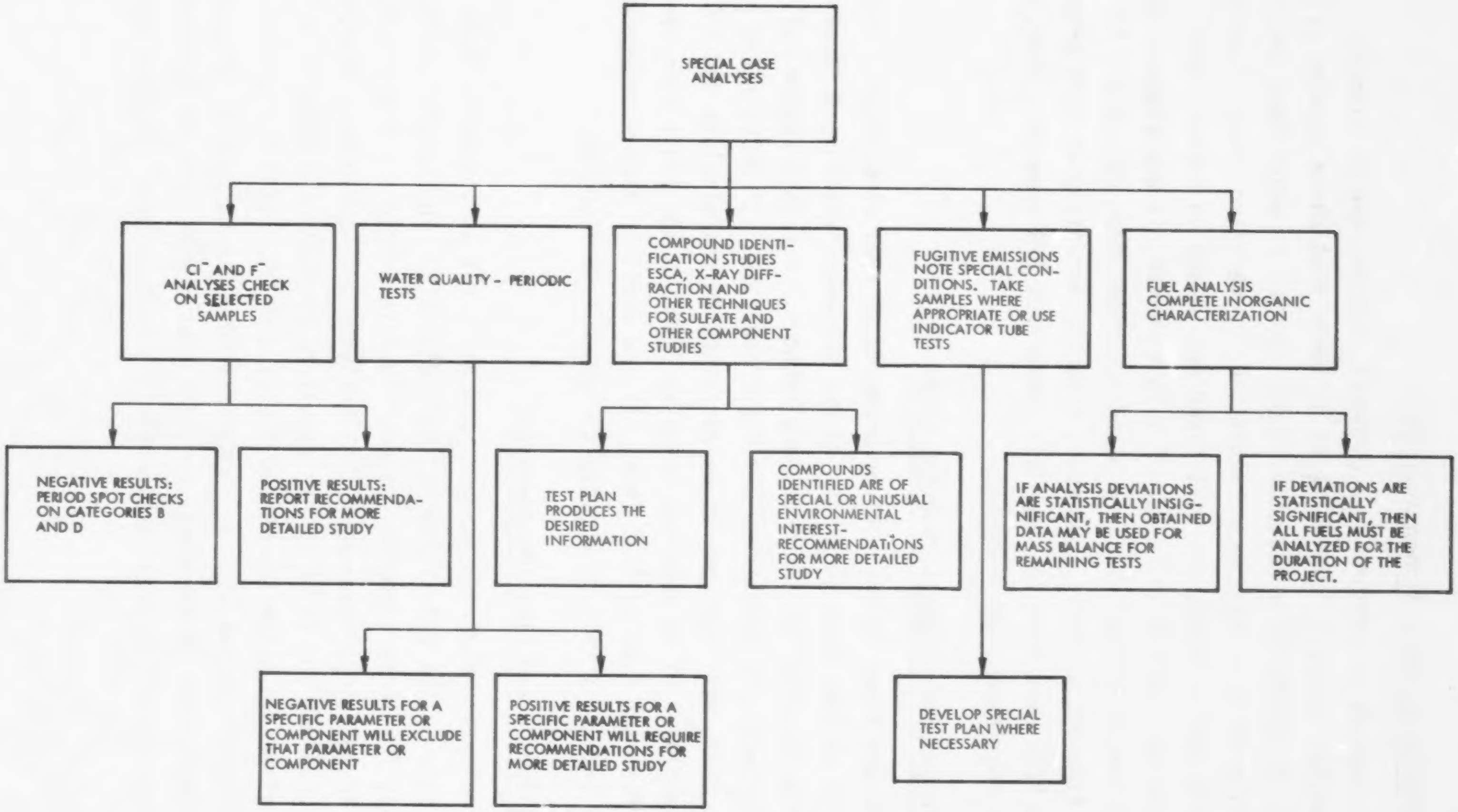

SPECIAL CASE ANALYSES
Cl^- AND F^- ANALYSES CHECK ON SELECTED SAMPLES
WATER QUALITY - PERIODIC TESTS
COMPOUND IDENTIFICATION STUDIES ESCA, X-RAY DIFFRACTION AND OTHER TECHNIQUES FOR SULFATE AND OTHER COMPONENT STUDIES
FUGITIVE EMISSIONS NOTE SPECIAL CONDITIONS. TAKE SAMPLES WHERE APPROPRIATE OR USE INDICATOR TUBE TESTS
FUEL ANALYSIS COMPLETE INORGANIC CHARACTERIZATION
NEGATIVE RESULTS: PERIOD SPOT CHECKS ON CATEGORIES B AND D
POSITIVE RESULTS: REPORT RECOMMENDATIONS FOR MORE DETAILED STUDY
TEST PLAN PRODUCES THE DESIRED INFORMATION
COMPOUNDS IDENTIFIED ARE OF SPECIAL OR UNUSUAL ENVIRONMENTAL INTEREST-RECOMMENDATIONS FOR MORE DETAILED STUDY
IF ANALYSIS DEVIATIONS ARE STATISTICALLY INSIGNIFICANT, THEN OBTAINED DATA MAY BE USED FOR MASS BALANCE FOR REMAINING TESTS
IF DEVIATIONS ARE STATISTICALLY SIGNIFICANT, THEN ALL FUELS MUST BE ANALYZED FOR THE DURATION OF THE PROJECT.
NEGATIVE RESULTS FOR A SPECIFIC PARAMETER OR COMPONENT WILL EXCLUDE THAT PARAMETER OR COMPONENT
POSITIVE RESULTS FOR A SPECIFIC PARAMETER OR COMPONENT WILL REQUIRE RECOMMENDATIONS FOR MORE DETAILED STUDY
DEVELOP SPECIAL TEST PLAN WHERE NECESSARY

Figure 3-3. Special Case Analysis Plan

3.4.1 Polychlorinated Biphenyls (PCB)

The various polychlorinated biphenyl species are of current environmental interest. While it is unlikely that these species will be found in any appreciable quantity, those samples in which they are the most likely to occur have been identified for detailed study. Complexity category B and D systems are coal fired and, based on current data, are likely sources for PCB analysis. For this reason, it was planned to select three sites from category B and two sites from category D for initial PCB sampling and analysis. However, from the inception of this program to date, no PCBs have been found on any concurrent EPA program. Thus, the PCB analysis requirement was dropped.

3.4.2 Polynuclear Organic Material (POM)

POMs are known to exist as by-products of coal combustion. These combustion systems have been studied but the exact extent and range of their emissions are for the most part unknown. For this reason, all sample extracts are identified for GC/MS analysis. If results are positive for POM, GC/MS will continue to be performed for particulate and XAD-2 module samples. If no POMs are found by GC/MS in the first five samples studied for each type of fuel (gas, oil and coal) or source category, the analysis intensity will be reduced to periodic spot checks.

3.4.3 Chloride and Fluoride Analysis

Chloride and fluoride analysis are difficult to obtain by SSMS methods because the volatility of these elements. The special analysis techniques for these elements, as described in Sections 8.9 and 8.10, represent an additional cost over SSMS analysis and considering the available data on chloride and fluoride distributions in fuels and ash, it will not be cost effective to perform these analyses on all samples from all sites. A selection of samples will be chosen for complete Cl^- and F^- analysis. If the results are as expected, periodic spot checks will be continued. If the results are unique, recommendations will be made for more detailed study.

3.4.4 Water Quality Tests

Complexity category C and D sites are the only sources that are expected to generate aqueous samples requiring both traditional and the more complex Level 1 water quality testing. However, at present most of these sites are monitored for compliance to water quality standards by various federal, state, and local agencies. Thus, it is expected that the water quality data base will be sufficient to preclude extensive water testing. Thus, these tests will be limited to the following:

- All sites where water quality standards are not enforced.
- Three sites from each complexity category where standards are enforced.

Specific problem areas identified as a result of the water quality analyses will be isolated for additional study at the conclusion of the three site analyses. Periodic spot checks will then be performed on incoming samples to increase reliability of preliminary observations. This topic is treated in detail in Section 3.8.

3.4.5 Special Inorganic Compound Identification Studies

X-ray diffraction, scanning electron microscopy - electron dispersive X-ray spectrometry, electron spectroscopy for chemical analysis and other sophisticated instrumental techniques are used for inorganic compound characterization studies on particulate and solids. Although these are Level 2 techniques, present evidence indicates that the identification of the various species (especially sulfate) may be required on sites from each complexity category. Selected samples will be used for more detailed compound identification testing based on the Level 1 results and program data needs.

Because much of this technology is state of the art and also the subject of special investigation under another contract at TRW (EPA Contract 68-02-2165), a separate test plan will be prepared at a later date utilizing the results of this program and/or integrating the two programs subject to the approval of the respective project officers.

3.4.6 Fugitive Emissions Studies

It is expected that fugitive emission data will be required mainly for those coal fired source categories assigned to complexity categories B and D and to a lesser extent to those large scale oil fired sources assigned to complexity category C. Because complex and detailed fugitive emission studies are presently being carried out by IERL for those types of combustion sources, it is anticipated that these studies will supply the data necessary for this program.

Each field test crew will be supplied with a set of indicator tubes to measure gaseous species where known problems exist or are expected to exist. (e.g., tests for SO_x, NO_x, and CO_2 in the furnace rooms of boilers with positive pressure.)

3.4.7 Fuel Feed Analysis

In order to obtain mass emission data, a reliable analysis of the fuel feed stock is required. It is expected that feed stocks will differ enough from site to site that individual analyses will be required on a per site basis. In the event that component differences between like fuel feeds are not significant enough to negatively impact mass emission determinations, a sufficient number of fuels will be analyzed to provide a reliable data base. If this data base can be established, fuel feed analysis will be terminated.

3.5 ANALYSIS CRITERIA FOR LIMITED QUANTITIES OF PARTICULATE SAMPLES

Figures 3-4 and 3-5 illustrate the analysis planning criteria for those flue gas samples which are limited in quantity due to a low grain loading of the flue gas. In this scheme, inorganic analysis always has first priority. In those samples where quantity is extremely limited, SSMS only will be performed. Particulate samples from sources with a grain loading of less than 0.01 grain/SCF will not normally be analyzed. In systems where grain loading is high enough to produce a sufficient quantity of particulate to warrant solvent extraction for organic material, the removal of 5% of the catch for inorganics will not significantly impact the analysis results.

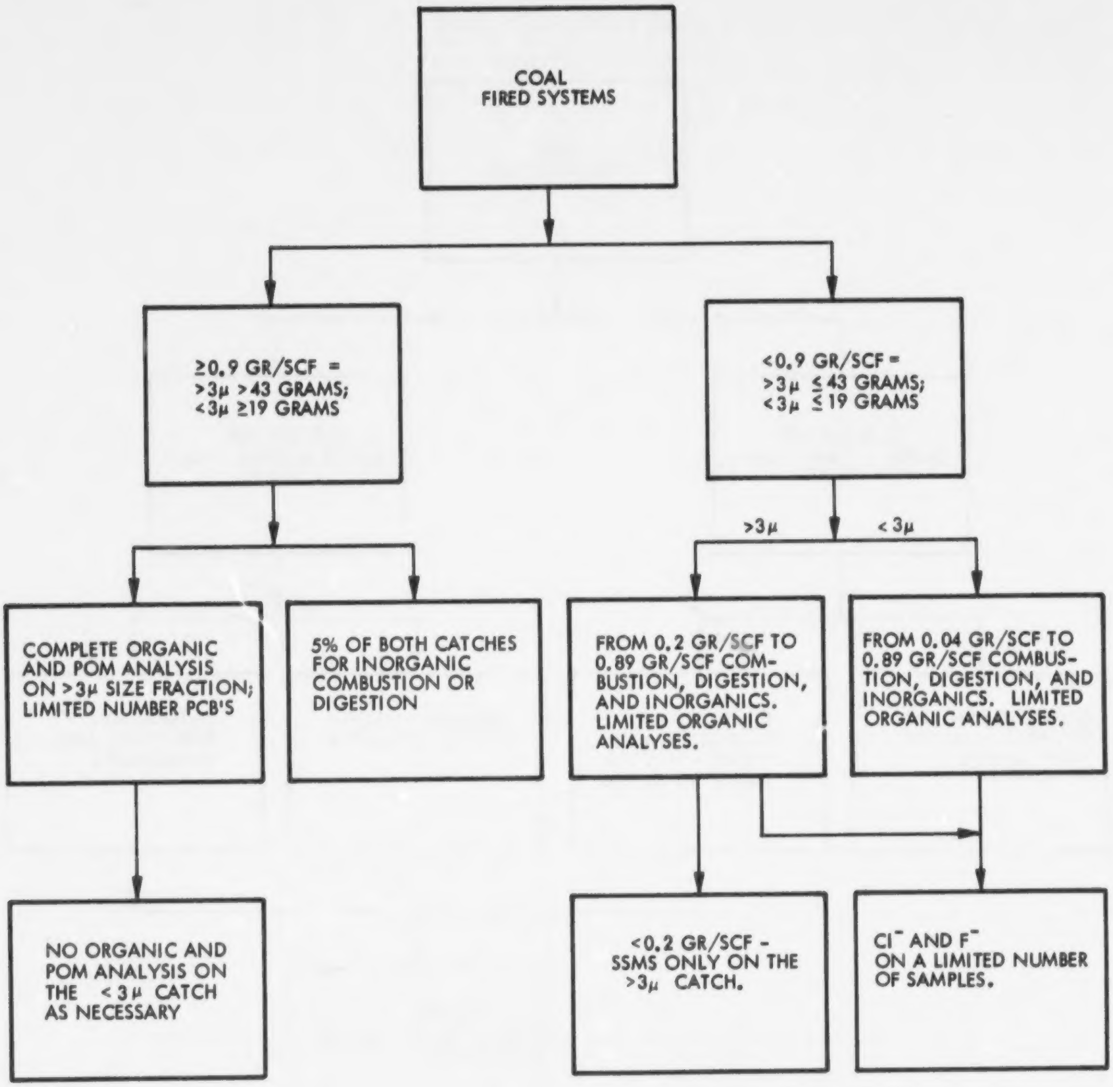

COAL FIRED SYSTEMS
≥0.9 GR/SCF = >3μ >43 GRAMS; <3μ ≥19 GRAMS
<0.9 GR/SCF = >3μ ≤43 GRAMS; <3μ ≤19 GRAMS
>3μ
<3μ
COMPLETE ORGANIC AND POM ANALYSIS ON >3μ SIZE FRACTION; LIMITED NUMBER PCB'S
5% OF BOTH CATCHES FOR INORGANIC COMBUSTION OR DIGESTION
FROM 0.2 GR/SCF TO 0.89 GR/SCF COMBUSTION, DIGESTION, AND INORGANICS. LIMITED ORGANIC ANALYSES.
FROM 0.04 GR/SCF TO 0.89 GR/SCF COMBUSTION, DIGESTION, AND INORGANICS. LIMITED ORGANIC ANALYSES.
NO ORGANIC AND POM ANALYSIS ON THE <3μ CATCH AS NECESSARY
<0.2 GR/SCF - SSMS ONLY ON THE >3μ CATCH.
Cl⁻ AND F⁻ ON A LIMITED NUMBER OF SAMPLES.

Figure 3-4. Particulate Analysis Decision Criteria for Coal Fired Systems

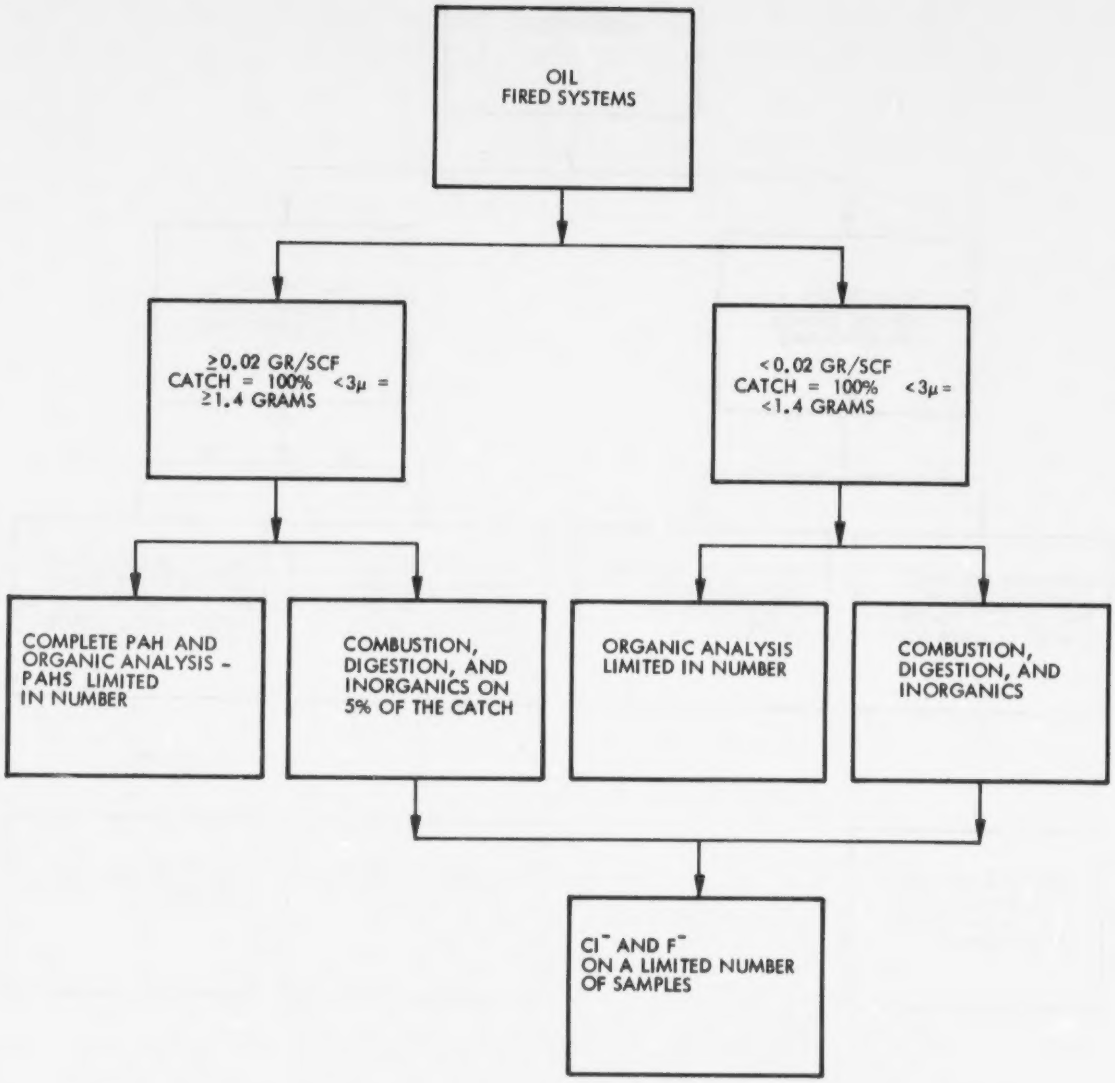

OIL
FIRED SYSTEMS
≥0.02 GR/SCF
CATCH = 100% <3μ =
≥1.4 GRAMS
<0.02 GR/SCF
CATCH = 100% <3μ =
<1.4 GRAMS
COMPLETE PAH AND ORGANIC ANALYSIS - PAHS LIMITED IN NUMBER
COMBUSTION, DIGESTION, AND INORGANICS ON 5% OF THE CATCH
ORGANIC ANALYSIS LIMITED IN NUMBER
COMBUSTION, DIGESTION, AND INORGANICS
Cl⁻ AND F⁻ ON A LIMITED NUMBER OF SAMPLES

Figure 3-5. XAD-2 Module Analysis Decision Criteria for Oil Fired Systems

3.6 ANALYSIS CRITERIA FOR XAD-2 MODULE SAMPLES

The XAD-2 module produces several samples that must be analyzed both for inorganic and organic components. Because individual analysis of samples is neither necessary nor cost effective, these samples are combined and analyzed once for inorganic and organic components as shown in Figures 3-6 and 3-7. Figure 3-8 shows the inorganic analysis scheme effective after EPA approval (after September, 1978).

3.7 PLANNING AND ANALYSIS CRITERIA FOR ORGANIC COMPONENTS

The analysis of samples for organic components is a very complex and cost sensitive area and for this reason a high degree of effort will be expended in the planning and tracking of samples for organic analysis. Generally speaking, all SASS train rinses and extractable samples such as particulates, XAD-2 resin and condensate, water, bottom ash, and slurries will be extracted and analyzed for organics unless experience or the organic analysis decision criteria indicates termination of the analysis procedure. Because fuels have been extensively analyzed for organic components, no analysis of these components will be performed unless a direct link between fuel composition and fuel gas emission is suspected.

3.7.1 General Organic Decision Criteria

The area of organic analysis is unique in that several decision points are an integral part of the procedure and must be applied by the analyst as an integral part of the procedure. In this revision, the detailed application of these criteria is included in Chapter 7. A summary of these decision points/criteria is given in Table 3-5.

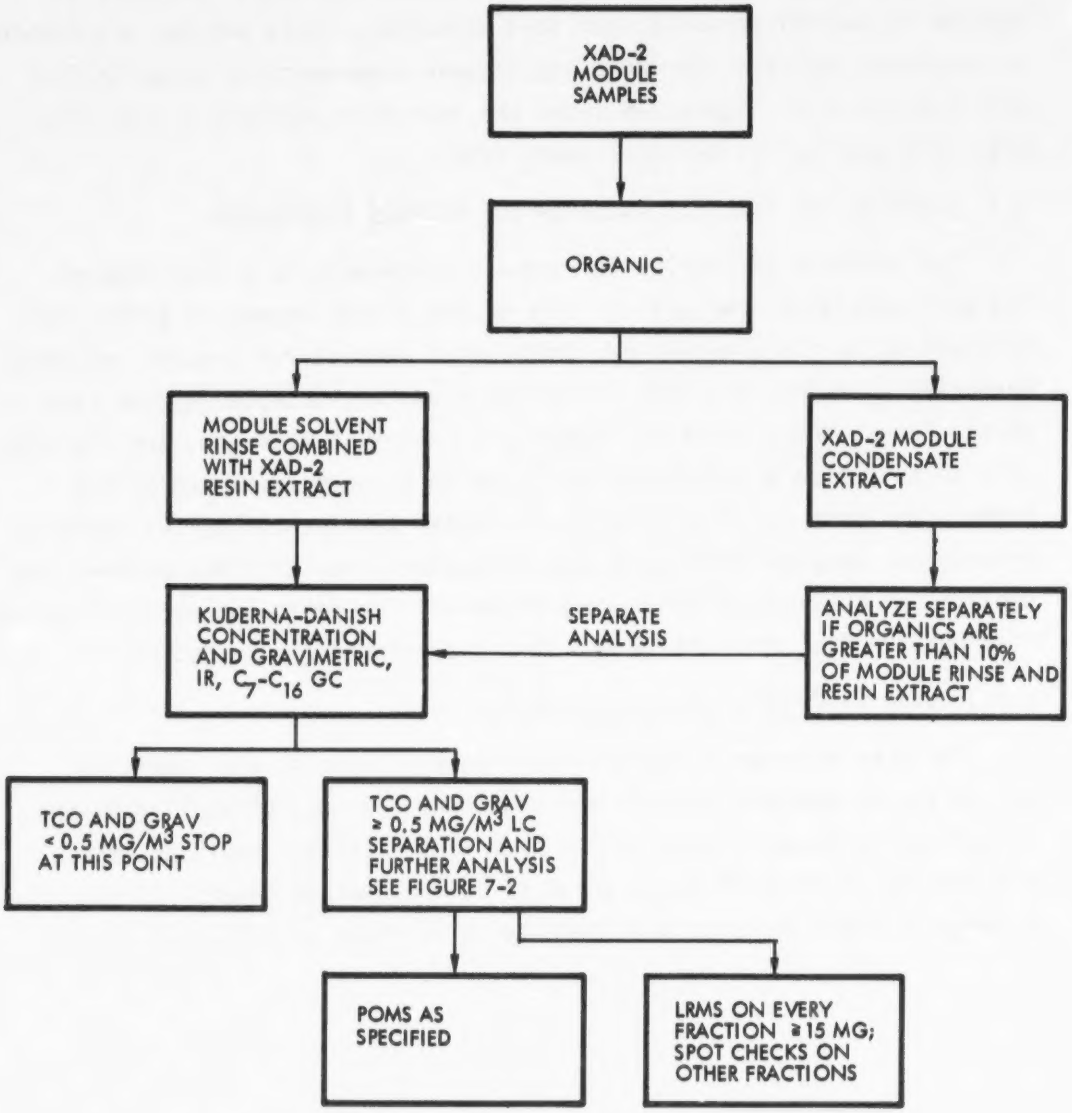

XAD-2 MODULE SAMPLES
ORGANIC
MODULE SOLVENT RINSE COMBINED WITH XAD-2 RESIN EXTRACT
XAD-2 MODULE CONDENSATE EXTRACT
KUDERNA-DANISH CONCENTRATION AND GRAVIMETRIC, IR, C7-C16 GC
SEPARATE ANALYSIS
ANALYZE SEPARATELY IF ORGANICS ARE GREATER THAN 10% OF MODULE RINSE AND RESIN EXTRACT
TCO AND GRAV < 0.5 MG/M3 STOP AT THIS POINT
TCO AND GRAV ≥ 0.5 MG/M3 LC SEPARATION AND FURTHER ANALYSIS SEE FIGURE 7-2
POMS AS SPECIFIED
LRMS ON EVERY FRACTION ≥15 MG; SPOT CHECKS ON OTHER FRACTIONS

Figure 3-6. XAD-2 Module Organic Analysis
Decision Criteria

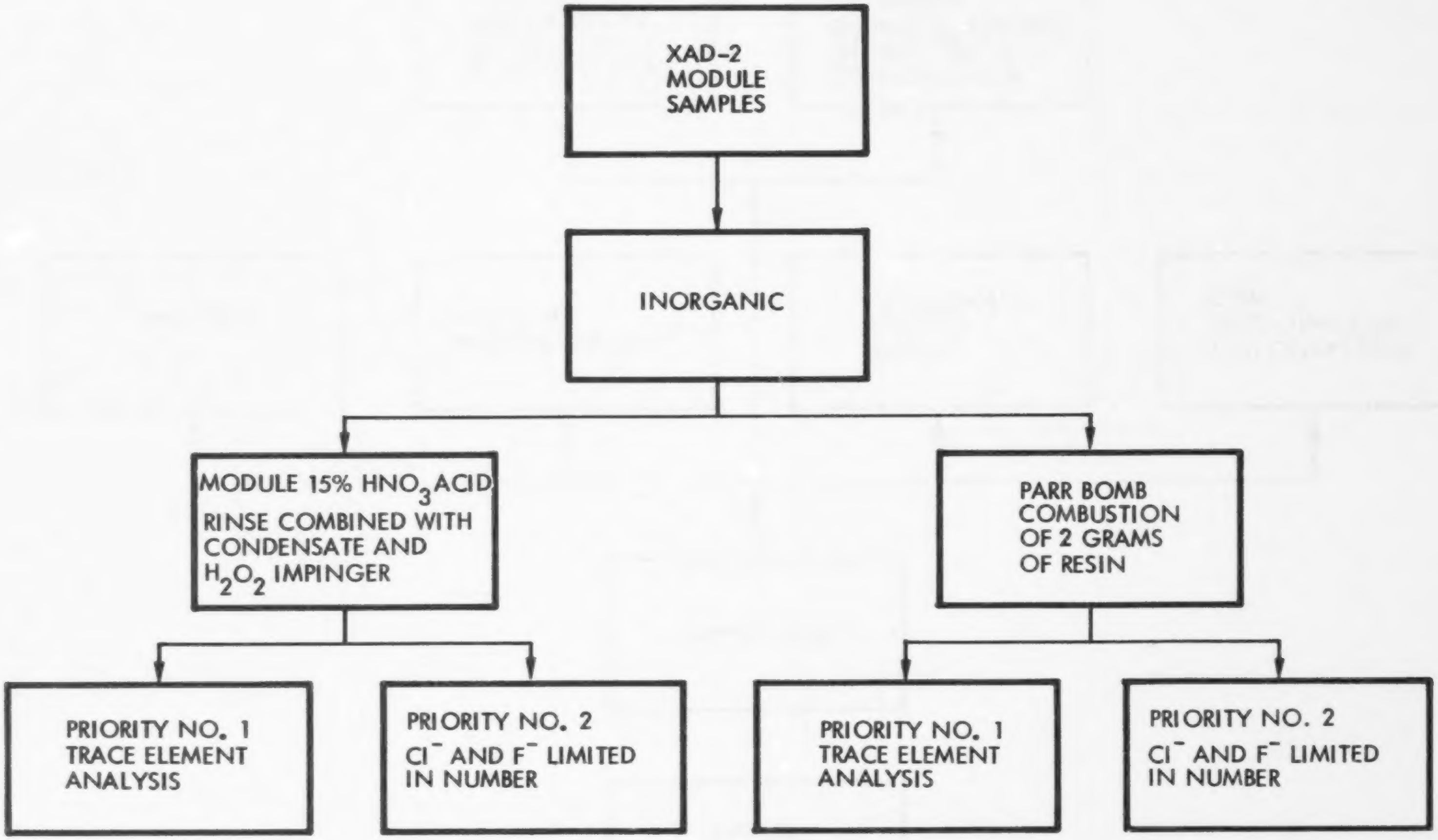

XAD-2
MODULE
SAMPLES
INORGANIC
MODULE 15% HNO_3 ACID
RINSE COMBINED WITH
CONDENSATE AND
H_2O_2 IMPINGER
PARR BOMB
COMBUSTION
OF 2 GRAMS
OF RESIN
PRIORITY NO. 1
TRACE ELEMENT
ANALYSIS
PRIORITY NO. 2
Cl^- AND F^- LIMITED
IN NUMBER
PRIORITY NO. 1
TRACE ELEMENT
ANALYSIS
PRIORITY NO. 2
Cl^- AND F^- LIMITED
IN NUMBER

Figure 3-7. XAD-2 Module Inorganic Analysis Decision Criteria

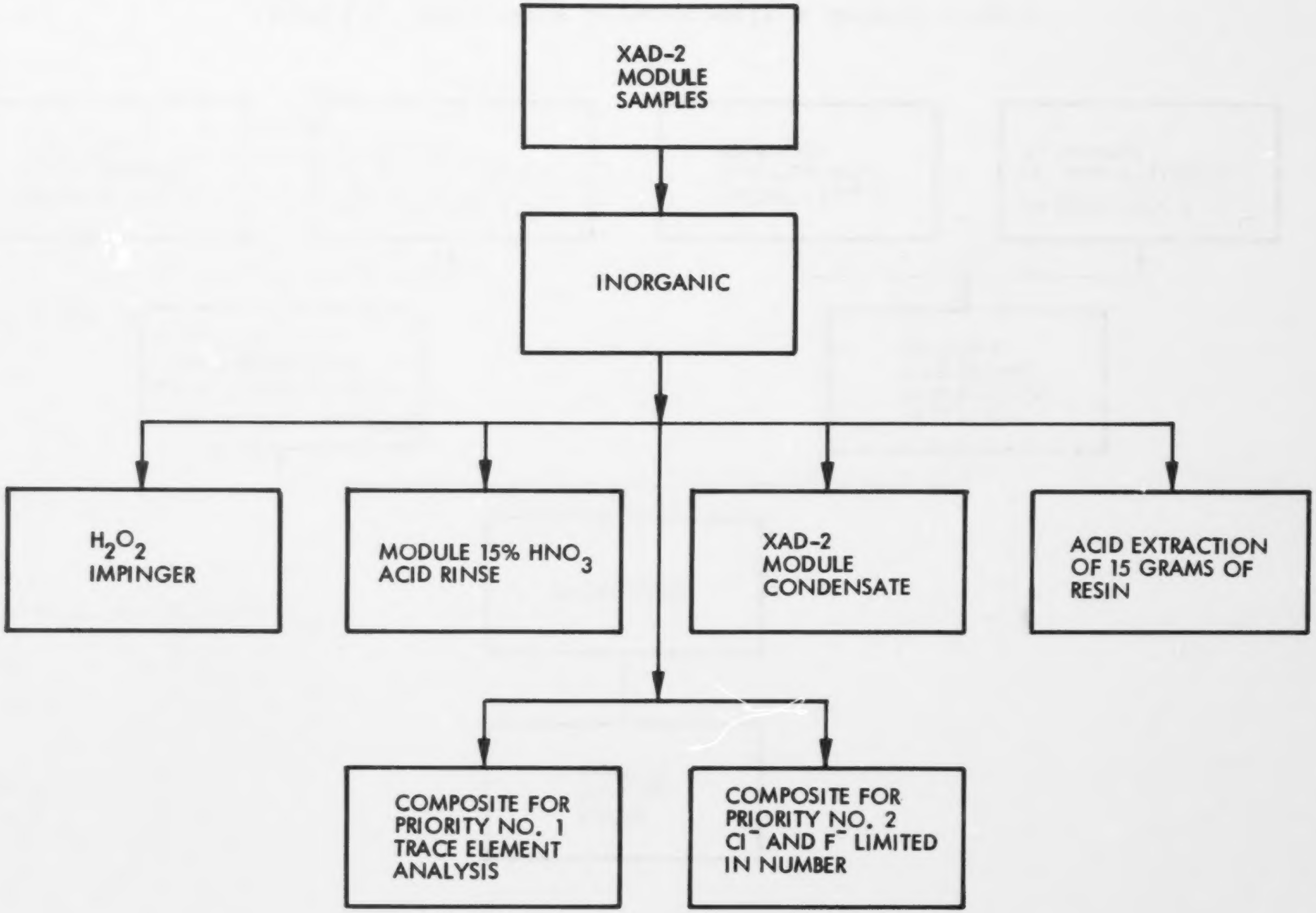

XAD-2 MODULE SAMPLES
INORGANIC
H_2O_2 IMPINGER
MODULE 15% HNO_3 ACID RINSE
XAD-2 MODULE CONDENSATE
ACID EXTRACTION OF 15 GRAMS OF RESIN
COMPOSITE FOR PRIORITY NO. 1 TRACE ELEMENT ANALYSIS
COMPOSITE FOR PRIORITY NO. 2 Cl^- AND F^- LIMITED IN NUMBER

Figure 3-8. XAD-2 Module Inorganic Analysis Decision Criteria Pending EPA Approval

Table 3-5. Organic Analysis Decision Points

Decision Point	Description	Section
Initial Extraction	Organic analysis omitted if quantity of particulate catch is limited and/or meets certain criteria (see below).	3.5
Gravimetric Analysis	a) Analysis terminated if organics concentration is <0.5 mg/m^3 b) Analysis on the XAD-2 condensate is discontinued if nonvolatile matter <10% of total organics or <0.5 mg/m^3.	7.5
Total Chromatographable Organics, C_7-C_{16} (TCO)	Simplified liquid chromatographic (LC) separation used if TCO <10% total organics.	7.7, 7.8
Infrared Analysis	Analysis not run on less than 0.5 mg for basic gravimetric residues and for LC fractions.	7.6
Low Resolution Mass Spectroscopy	Run only on total residues of LC fractions, if present in concentrations of >0.5 mg/m^3.	7.6, 7.9
POM Analysis	Performed only on all fractions.	7.10

3.7.2 Prediction of Quantity of Organic Material in Particulate Catches

The organic analysis planning and decision criteria is being emphasized for particulate samples because these samples represent a large proportion of the total sample collected. Significant cost savings with no loss in technical quality can be realized if samples that will not meet the Level 1 organic analysis criteria (i.e., <0.5 mg/m^3) can be eliminated without the expenditure of significant quantities of labor. However, program requirements to analyze all extracts for POMs, the lack of $>3\mu$ particulate in all cases where the source was controlled, and the generally very low amounts of $<3\mu$ particulate has resulted in little need for the prediction criteria presented in earlier draft version of the manual. Thus, the nomograph and the remaining parts of the section have been deleted.

3.8 WATER SAMPLING AND ANALYSIS PROTOCOL

3.8.1 Sampling Wastewater Emissions

The major wastewater emissions from stationary combustion sources are described in Table 3-6. These wastewater emissions are similar in characteristics for the utility and industrial sectors, and insignificant or nonexistent in terms of total quantities discharged for the commercial/institutional and residential sectors. An adequate characterization of the wastewater emissions from the utility sector is therefore considered adequate for all combustion source types.

Table 3-6. Wastewater Emissions from Stationary Combustion Sources

Unit Operation	Fuel			
	Coal	Resid Oil	Distillate Oil	Gas
Fly ash pond discharge	S	MS	MS	NA
Bottom ash pond discharge	S	MS	MS	NA
Coal pile drainage	S	NA	NA	NA
Cooling system waste	IS	IS	IS	IS
Boiler blowdown	IS	IS	IS	IS
Water treatment	IS	IS	IS	IS
Equipment cleaning	IS	IS	IS	IS
Desulfurization Wastewater	S	S	S	NA

S = source

MS = minor source

IS = sources for which wastewater characteristics are independent of type of fuel burned.

NA = not applicable

As discussed in Reference 5, review of recent and current combustion system studies indicates that there are a number of parallel projects that are directed towards the characterization of wastewater emissions from power plants. Specifically, these projects include:

1) A current TVA study (EPA-IAG-D5-E721, TV-41967A) to characterize coal pile drainage, ash pond discharges, chlorinated once-through cooling water discharge, and chemical cleaning wastes from periodic boiling-tube cleaning to remove scales. The TVA program samples and analyzes the waste water emissions from TVA owned coal burning power plants. The TVA power plants are either of the pulverized dry bottom or the cyclone variety.
2) A current study conducted by Hittman Associates to characterize ash handling and material storage wastes from four coal burning power plants (lignite, subbituminous, and bituminous coal), cooling system wastes from eight power plants (once through and recirculative system, fresh and saline water), copper boiler wastes from two power plants, and low volume wastes (such as equipment cleaning wastes) from two power plants.
3) Current and recent studies conducted by the Aerospace Corporation to provide data on the characteristics of wastewater emissions from flue gas desulfurization systems. The four systems from which scrubber liquors were analyzed included the EPA/TVA Shawnee steam plant venturi and spray tower, the EPA/TVA Shawnee steam plant turbulent contact absorber, the Arizona Public Service Cholla Station flooded disc scrubber and absorption tower, and the Duquesne Light Phillips Station single and dual stage venturi.

Our analysis of currently available information, however, shows, a number of areas where there are significant data gaps. In summary, the following conclusions have been reached:

- Adequate emissions data for coal pile drainage will be available from the TVA program.
- Emissions data for water treatment wastes are considered adequate because both the quantity and the characteristics of the water treatment wastes can be estimated with reasonable accuracy from mass balance calculations.
- Emissions data for cooling system wastewater, equipment cleaning wastewater, desulfurization wastewater and boiler blowdown are limited.
- Emissions data for ash pond discharges are adequate for bituminous pulverized dry bottom boilers and inadequate for other types of coal-fired boilers, and also inadequate for resid oil fired boilers.

Based on the above conclusions, the present sampling plan for wastewater emissions are as follows:

Unit Operations	No. of Test Sites
Ash Pond Discharge	
Bituminous Wet Bottom	5
Bituminous Cyclone	2
Bituminous Stoker	1
Lignite Pulv. Dry Bottom	2
Lignite Cyclone	2
Lignite Stoker	1
Resid Oil	5
Cooling Tower Blowdown	2-5
Once through Cooling System	2-5
Boiler Blowdown	3-5
Equipment Cleanup	2-5
Desulfurization Wastewater	2-5

3.8.2 Analysis

Due to the large number and quantity of samples required for analysis and the potential for sample degradation during shipment, most of the standard waste water analyses will be performed in the fields by the Hach analysis methods as described in Chapter 6. BOD and COD analysis were thoroughly investigated, and it was found out that these results were not necessary. A summary of the water analyses to be performed is given in Table 3-7.

Table 3-7. Liquid Stream Sampling and Analysis Protocol

General Information						Sampling Locations and Analysis Requirements			
Parameters to be Analyzed	Analysis Location		Volume Sample Required	Method of Analysis	Sample Preservation Required	Type A Ash Ponds	Type B Cooling H_2O Blowdown	Type C Cleaning Waste	Comments
	Field	Lab							
Flow	F		1 liter	Plant Meter or Bucket/Stopwatch	None	X	X	X	
pH	F			Portable Meter		X	X	X	
Cond	F			Hach Kit		X	X	X	
TSS	F			Hach Kit		X	X		
Hardness	F			Hach Kit		X			
Alk. or Acid	F			Hach Kit		X			
$NH_3 \cdot N$	F			Hach Kit		X			May be discontinued later on
Cyanide	F			Hach Kit		X	X	X	May be discontinued later on
NO_3-N	F			Hach Kit		X			
PO_4-P	F			Hach Kit		X	X		
SO_3	F			Hach Kit		X			
SO_4	F			Hach Kit		X			
Cl		L	200 ml	Specific ion Electrode		X			
F		L				X		X	
Ca		L	800 ml		0.1N HNO_3 to pH 2	X		X	
Mg		L		SSMS		X		X	
K		L				X		X	
Na		L				X			
Other Trace Elements		L				X	Cr (Total)	X	
Total Organics		L		GC-TCO and Gravimetric	CH_2Cl_2 Ext Amber Bottle with Teflon Seal	X	X	X	
PAH		L	1ℓ Organic CH_2Cl_2 Extract	GC/MS		X	X	X	May be discontinued later on
PCB		L		GC/MS		X	X	X	
Other Organics		L				X		X	

3.9 SPECIAL ANALYSIS CRITERIA FOR GAS, DISTILLATE OIL AND RESIDUAL OIL COMBUSTION SOURCES

The available literature and program experience had indicated that a complete Level 1 analysis of gas, distillate oil, and residual oil combustion sources was not providing meaningful data due to the very low levels of particulate and organic material present. Specifically, the various Level 1 analysis for the different samples from the SASS train were either giving negative results or results with high variance due to low levels present. Thus, for these sources a series of analysis deletions, and sample combinations were proposed in order to reduce analysis costs and increase data precision and accuracy for these sites. These were implemented as a directed contract change after June 7, 1978. They are listed below.

- Natural Gas Fired Sites
  a) Eliminate all inorganic analysis on SASS train samples.
  b) Combine all SASS train organic extracts and rinses into a single sample before analysis.
- Distillate and Residual Oil Fired Sites
  a) Compute inorganic emissions from fuel analysis assuming 100% emissions.
  b) Eliminate all inorganic analysis on SASS train samples.
  c) Combine all SASS train organic extracts and rinses into a single sample before analysis.

3.10 REFERENCES

1) C. A. Zee, et al, "Evaluation of the SASS Train and Level 1 Sampling and Analysis Procedures Manual", TRW Contract No. 68-02-2165 Task 5, Redondo Beach, Ca.

2) S. L. Reynolds, et al, "SASS Train and Level 1 Procedures Evaluation" TRW Contract No. 68-02-2165 Task 14, Redondo Beach, Ca.

3) Norman Surprenant, et al, "Preliminary Emissions Assessment of Conventional Stationary Combustion Systems, Volume II", Contract No. 68-02-1316 Task 2, GCA Corporation, Bedford, Mass.

4) A. E. Vandegrift, et al, "Particulate Pollutant System Study", Vol. 1, 2 and 3, Contract No. 22-69-104, Midwest Research Institute, Kansas City, Mo.

5) C. C. Shih to B. J. Matthews. Emissions Data Needed from Field Sampling and Analysis Efforts. IOC 4342.5-77-009. 1 February 1977.

4.0 SAMPLE AND DATA MANAGEMENT

The sample and data management function will involve the Sample Bank Manager along with the Laboratory Operations Manager and will provide interfacing and support in several key areas:

- Receiving field samples
- Maintaining a sample bank
- Relating field results to laboratory decisions
- Disbursing samples to analysts
- Tracking and controlling sample flow
- Collecting and reducing analytical data
- Preparing reports of analytical data

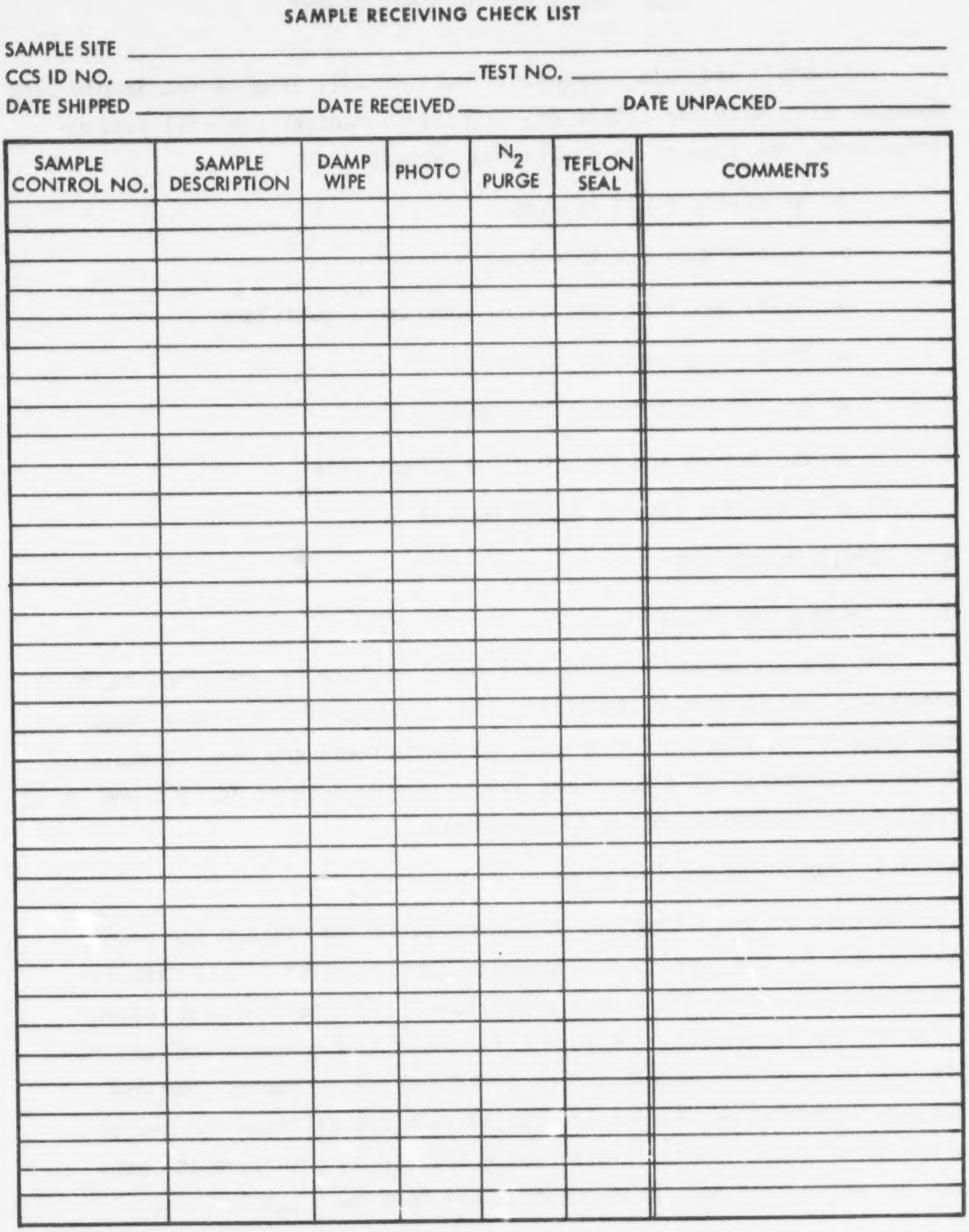
4.1 SAMPLE MANAGEMENT

4.1.1 Sample Receiving

The inspection and logging of samples as they are received is, in essence, a quality control measure. The shipment of field data forms and samples are checked for procedural correctness and completeness, field measurements of volumes and weight are remeasured for QC, and solid samples are photographed for documentation.

4.1.1.1 Unpacking and Inventory

An area of the laboratory is dedicated and maintained for sample receiving. As the samples are unpacked, the exterior of the sample containers is wiped with a damp paper towel. The samples are logged in using the form shown in Figure 4-1. Notes and comments written on the sample container labels are recorded and solid samples that are subject to oxidative changes are purged with dry nitrogen and sealed with Teflon tape. There is also space allowed on this form to note samples which have been photographed (see Section 4.1.1.3).



SAMPLE RECEIVING CHECK LIST

SAMPLE SITE ____________________

CCS ID NO. ____________________ TEST NO. ____________________

DATE SHIPPED ______________ DATE RECEIVED ______________ DATE UNPACKED ______________

SAMPLE CONTROL NO.	SAMPLE DESCRIPTION	DAMP WIPE	PHOTO	N_2 PURGE	TEFLON SEAL	COMMENTS

Figure 4-1. Sample Receiving Check List

4.1.1.2 Quality Control Check

To verify the quality of the recorded field data, selected samples from each shipment will be checked for the following critical parameters:

- Sample collection weight
- Sample volume
- pH value from a field fixing operation
- Type of container used

For this check, the form shown in Figure 4-2 will be used. Collection weights will be checked on cyclone catch samples. Volumes will be checked on all solvent samples (hardware rinses and liquid extractions), acid XAD-2 module rinses, and impinger liquids. Samples that have had acidic splits prepared (bulk liquids and XAD-2 module condensates) will be checked for pH. This work is to be done in the Cleanroom area at TRW (01/2031) and in an equivalent facility at GCA.

4.1.1.3 Photography

Photographs of the SASS train filters will be taken to document the "as received" condition of the samples and general gross characteristics. Photomicrography will then be conducted on filter samples or solid samples designated by the Laboratory Operations Manager to observe and record finer structural characteristics. Magnifications from 30X to 600X will be used to examine the samples. The microscopic work will also be conducted in the Cleanroom area at TRW (01/2031) and in an equivalent facility at GCA.

4.1.2 Sample Bank and Storage

The sample bank consists of a centralized locked storage area to which only the Sample Bank Manager and his designees have access. Cabinets for active storage will be located at TRW and at GCA. Long term storage for both TRW and GCA samples will be maintained at TRW. These facilities assure that the temperature, humidity and light exposure will be maintained within a constant range. (Temperature 65-75°F, relative humidity 20-40% and storage in the dark). Organic samples resulting from solvent rinses and extractions will be stored in explosion-proof refrigerators to preserve sample integrity and minimize solvent loses.

SAMPLE RECEIVING QC

SAMPLE SITE ______________________________
CCS ID NO. ____________________ TEST NO. ____________________
QC CHECK PERFORMED ON (DATE): ____________, BY (SIGNATURE): ____________________

SAMPLE CONTROL NO.	TYPE OF CONTAINER	WEIGHT (g)		VOLUME (ml)		pH		COMMENTS
		FIELD	LAB	FIELD	LAB	FIELD	LAB	

Figure 4-2. Sample Receiving QC

4.1.3 Sample Disbursement

The samples remain in active storage until the Laboratory Operations Manager directs the Sample Bank Manager to disburse the samples and a disbursement plan is agreed upon. The basic plan, as shown in Figure 4-3, will be followed for all facilities with adjustments and allocations determined by the decision criteria discussed in Chapter 3.

The actual manipulation which reduces the gross samples to representative aliquots for analysis must be conducted in the Cleanroom to prevent contamination. The issuing of aliquots will be done at one time as much as possible for ease of handling the divided samples and also to maintain consistency and integrity. The homogenizing and disbursement of each bulk sample and SASS train catch are discussed separately in the following paragraphs.

4.1.3.1 Bulk Liquid Samples

Bulk liquid samples are received in gallon (4-liter) containers and represent collected waste water, reservoir water, cooling water, evaporation pond water, the liquid portion of a slurry, or bulk fuel oil samples. The aqueous samples will have been extracted for organics with methylene chloride in the field. These solvent extracts proceed directly to the organic analysis scheme. The aqueous phase from the field extraction will have been split into acidic and neutral portions for trace metal, sulfate and anion analyses. Aliquots are taken by agitating the containers for 30 seconds and then pipeting the sample volume specified by the disbursement plan into a suitably cleaned container.

Aliquots of the bulk fuel oil samples for ultimate analysis, and Parr bomb combustion, and inorganic analyses are taken by simply pouring an unmeasured portion into a small, clean container and allowing the analyst to weigh out the precise sample amount needed.

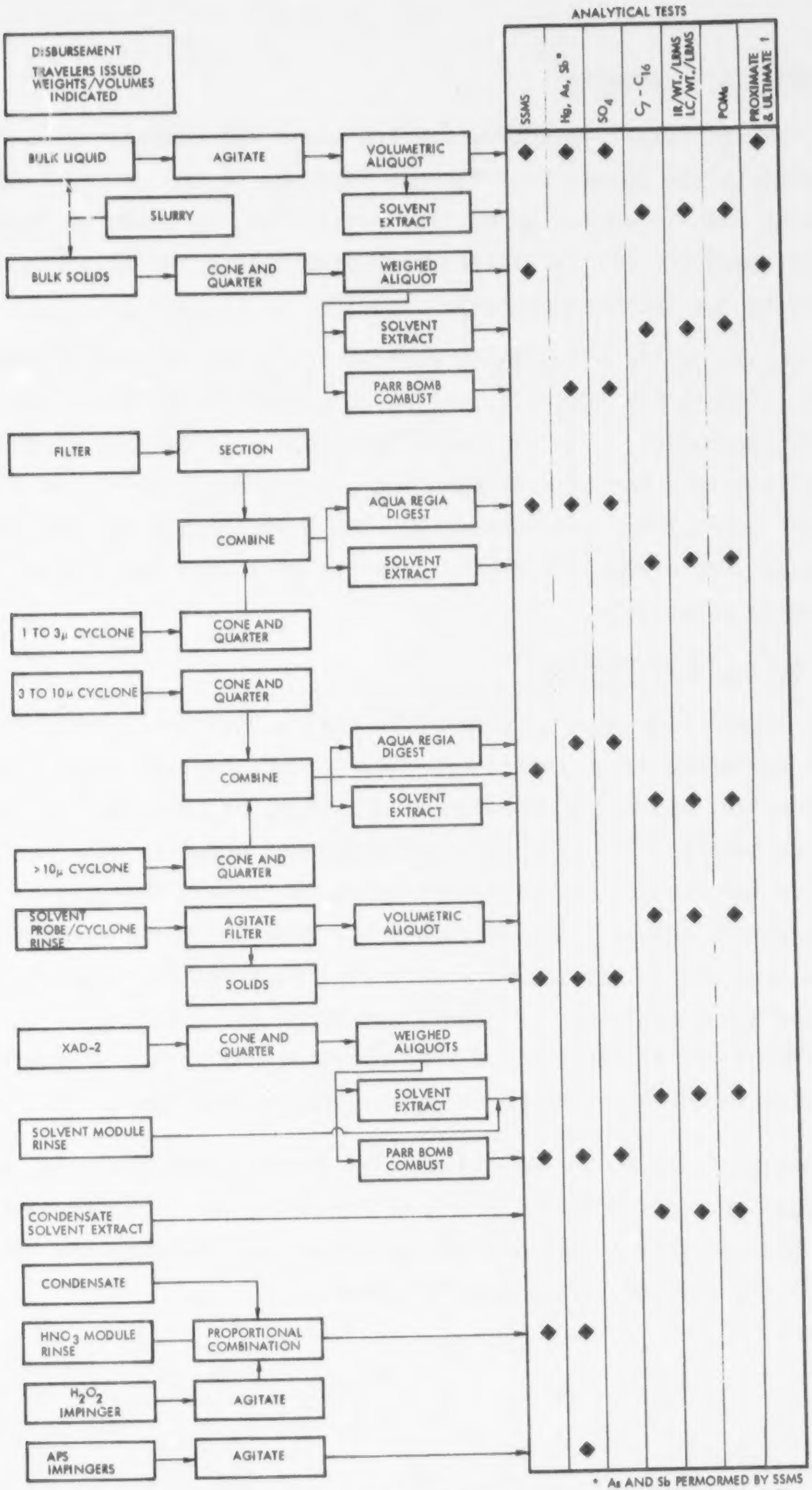

ANALYTICAL TESTS
SSMS
Hg, As, Sb*
SO4
C7 - C16
IR/WT./LRMS
LC/WT./LRMS
POMs
PROXIMATE & ULTIMATE †
DISBURSEMENT
TRAVELERS ISSUED
WEIGHTS/VOLUMES INDICATED
BULK LIQUID
AGITATE
VOLUMETRIC ALIQUOT
SLURRY
SOLVENT EXTRACT
BULK SOLIDS
CONE AND QUARTER
WEIGHED ALIQUOT
SOLVENT EXTRACT
PARR BOMB COMBUST
FILTER
SECTION
AQUA REGIA DIGEST
COMBINE
SOLVENT EXTRACT
1 TO 3μ CYCLONE
CONE AND QUARTER
3 TO 10μ CYCLONE
CONE AND QUARTER
AQUA REGIA DIGEST
COMBINE
SOLVENT EXTRACT
>10μ CYCLONE
CONE AND QUARTER
SOLVENT PROBE/CYCLONE RINSE
AGITATE FILTER
VOLUMETRIC ALIQUOT
SOLIDS
XAD-2
CONE AND QUARTER
WEIGHED ALIQUOTS
SOLVENT EXTRACT
SOLVENT MODULE RINSE
PARR BOMB COMBUST
CONDENSATE SOLVENT EXTRACT
CONDENSATE
HNO3 MODULE RINSE
PROPORTIONAL COMBINATION
H2O2 IMPINGER
AGITATE
APS IMPINGERS
AGITATE

Figure 4-3. Disbursement

* As AND Sb PERMORMED BY SSMS WHERE POSSIBLE AFTER 6/1/78

† FUEL SAMPLE ONLY

4.1.3.2 Bulk Solid Samples

Bulk solid samples are received in large jars, bags or cans and include ashes and fuels. They will be prepared for analysis by the ASTM coning and quartering procedure (Appendix D). This procedure shows in detail how to systematically divide a large sample into representative parts. Coning and quartering of all samples is to be conducted in the Cleanroom's laminar flow bench on a piece of precleaned Teflon sheet. The Sample Bank Manager is responsible for calculating from the reported bulk sample weight how many dividing steps must be performed to obtain the sample weight specified by the disbursement plan. In some cases, it may be necessary to obtain a fairly large portion, grind this to a finer mesh, and then proceed with the coning and quartering to obtain analytical size samples.

Bulk fuel samples will require disbursement of about 150 g for proximate and ultimate analysis and about 5 g for Parr bomb combustion and inorganic analysis. Other process solid samples (bottom ash, flyash, precipitate dusts, etc.) will be aliquoted for both organic and inorganic routine analyses. Special testing requested by the Laboratory Operations Manager, e.g., XRD or ESCA, will require disbursing additional aliquots.

4.1.3.3 Particulate Filters

Particulates, whether collected on a filter or in bulk, contain varying amounts of moisture. Before any sample is disbursed for analysis, it must be desiccated adequately to produce a constant sample weight. Each sample, in its open container, is placed in a desiccator containing Drierite for seven days. At the end of this period, the sample is weighed on an analytical balance to the nearest 0.1 mg. All samples are returned to the desiccator for an additional minimum of 24 hours. A series of at least four weighings is needed as a check of the accuracy and reproducibility of the original weight, although more may be needed. A standard deviation, s, of less than 10 mg is one criterion for deciding whether the average weight is stable. Applying a statistical test to the results to detect a gradual change in the average weight, or constant weight, is often required. The average variance between successive pairs of weighings, q^2, is compared with the overall variance of all weighings, s^2. The calculated ratio $q^2/s^2 = r$ can be compared with values in statistics tables. Weighings are continued and outlying value discarded until an acceptably low r value is obtained. Then the average weight is accepted as valid.

The quantity q is given by

$$q^2 = \frac{\sum^{n-1} Di^2}{(n-1)^2}$$

where

Di = difference between consecutive weighings

n = number of weighings

The filter collected sample typically cannot be representatively removed by mechanical methods. It is, therefore, sectioned using a precleaned knife. Sections are wedges produced by cutting along the diameter of the filter. The number of sections to be cut and their disbursement will depend on the type of source sampled and the weight of collected material as discussed in Chapter 3, Decision Criteria, and thus will be specified as part of each site's disbursement plan.

4.1.3.4 1 to 3 Micron Cyclone

The 1-3μ cyclone sample handling and disbursement parallels that of the filter, because these two samples are generally combined for analysis. For example, assume that the filter from a site test is disbursed 1/2 for organic solvent extraction and 1/4 for aqua regia extraction (with 1/4 held in reserve in the sample bank) and that the 100 ml aqua regia extract is in turn disbursed 80 ml for Hg and SO_4 and 20 ml for SSMS. To proportionally combine the 1-3μ cyclone catch, that sample would be disbursed 50% for organic solvent extraction, 20% for aqua regia extraction, and 5% for SSMS. After desiccation to constant weight, the cyclone catch is coned and quartered in the same manner as the bulk solid samples.

4.1.3.5 3-10 and >10 Micron Cyclones

After having been desiccated for a sufficient time to attain a constant weight (Section 4.1.3.3), these two cyclone samples are separately coned and quartered and then combined by a weight which represents an equal percentage of each. Portions are then disbursed for organic solvent extraction, aqua regia extraction, SSMS, and other special tests as necessary and as the quantity of sample available permits.

4.1.3.6 Solvent Probe/Cyclone Rinse

The solvent rinse of the probe and cyclones is filtered through a precleaned and tared Teflon Millipore filter, and the solvent filtrate is then disbursed for organic analysis. The filtered solids are desiccated and weighed; and if they are found to represent > 10% of the total particulate catch, they are disbursed for inorganic analyses by direct SSMS and aqua regia extraction for Hg and SO_4.

4.1.3.7 XAD-2 Resin

Resin samples are also coned and quartered, with the bulk of each sample going for solvent extraction. The only other aliquot taken is approximately 10 g, from which the sample for Parr bomb combustion is weighed, with the remainder being kept in the bank as a reserve. The solvent extract of the resin is subsequently combined with the solvent rinse of the XAD-2 module for organic analysis. The Parr bomb solution proceeds through the inorganic analysis as an integral sample without being combined with any other SASS samples.

This Procedure will be changed along with Figure 4.3, if the proposed procedure in Section 8.2 is approved by EPA. In order to provide adequate sample representation in the inorganic, organic and reserve sample aliquots, the following steps will have to be performed when the new procedure is adopted.

1. Keep the wet or dry XAD-2 resin in the original bottle as received from the field.
2. Stir the resin with a glass stirring rod. It is important that the resin is thoroughly mixed. Stir constantly for at least two minutes.

   After mixing, place the following aliquots in the indicated containers:

   a. 10 grams of resin in a 50 ml amber glass jar for Parr Bomb combustion and sample reserve.
   b. 15 grams of resin in a 50 ml amber glass jar for the proposed inorganic analysis.
   c. The remaining resin, ∿ 125 grams, in the original container received from the field for organic analysis.

4.1.3.8 XAD-2 Module Condensate

In the field, 90% of the condensate is extracted with methylene chloride. The unextracted portion of the aqueous phase from the extraction is then acidified. When these samples are received in the lab, they are disbursed as follows:

- Neat Extracted Condensate - no routine disbursement, this sample is held in the bank until a special analytical need is identified by the Laboratory Operations Manager.
- Methylene Chloride Extract - this sample is disbursed for organic analysis as an integral sample.
- Acidic Split - an aliquot proportional to the percentage of resin used for inorganic extraction, is combined with portions of the acid module rinse and the first impinger, and the resulting solution is disbursed for SSMS and Hg analyses.

4.1.3.9 XAD-2 Module Solvent Rinse

The solvent module rinse is proportionally combined with the extract of the XAD-2 resin and is then disbursed for organic analysis.

4.1.3.10 XAD-2 Module Acid Rinse

An acid module rinse aliquot proportional to the percentage of resin used for inorganic extraction, is combined with portions of the acidic condensate split and the first impinger solution, and inorganic extraction.* The resulting solution is disbursed for inorganic analyses as specified in each site's disbursement plan. The aliquot volume of each sample to be combined will also be specified in the disbursement plan.

4.1.3.11 First Impinger

A peroxide impinger volume proportional to the percentage of resin used for inorganic extraction is combined with portions of the acidic condensate split, the acid module rinse ard inorganic extract.* The resulting solution is disbursed for inorganic analyses as specified in each site's disbursement plan. The aliquot volume of each sample to be combined will also be specified in the disbursement plan.

4.1.3.12 Second and Third Impingers

An aliquot of the combined second and third (ammonium persulfate) impinger solutions is disbursed for Hg, As, and Sb analyses.

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* This presumes approval of the procedure in Section 8.2.

4.1.4 Sample Coding

The sample coding system to be used in this program is outlined in Figure 4-4. This system will be used to label and identify samples from the time they are taken in the field through all laboratory analyses. The sample control numbers derived through this coding system will appear on all container labels, analytical travelers, and analytical schedule flow control charts. Key aspects of the coding system worth noting are:

- The assigned numbers shown in the attached figure cover only the samples and procedures that are currently expected to be part of most, if not all, Level 1 tests. Additional numbers can be assigned to identify optional and Level 2 samples and procedures.
- Sample types 1, 2, 7, and 8 do not necessarily have to be separated slurries, but if slurries are encountered these are the code numbers that should be used for them.
- If more than one particulate filter is used in a test, the letters, a, b, c, etc. can be added to the sample type code to identify the multiple samples.
- Samples disbursed from the sample bank will be labeled with the sample control number identifying the next procedure to be performed. For example, an XAD-2 sample (from the first site sampled by the TRW east coast team) for Parr bomb combustion will have the sample control number 200-XR-PB. After the combustion, an aliquot of that sample for sulfate analysis will be labeled 200-XR-PB-SO4.
- Samples that are combined for certain analyses will acquire a new sample type code in their subsequent sample control numbers. For example, when the XAD-2 resin extract and the solvent module rinse (from the second site sampled by the TRW west coast team) are combined for Kuderna-Danish concentration, the sample control number that will be on the sample container and analytical traveler will be 101-XM-SE-KD.

4.1.5 Sample Tracking

Samples are tracked by using a combination of analytical traveler worksheets, weekly and monthly summary reports, and analytical schedule flow control charts. The traveler worksheets are issued by the Sample Bank Manager along with the samples and they contain all pertinent information needed by the analyst (volume, matrix, etc.) as well as space for the analyst to record his data. A copy of the issued traveler

XXX-XX-XX-XXX-XX-X

SITE IDENTIFICATION	SAMPLE TYPE	SAMPLE PREPARATION	FIRST LEVEL ANALYSIS		SECOND LEVEL ANALYSIS	THIRD LEVEL ANALYSIS
Consecutively numbered by sampling team:	Numbers and corresponding sample types are as follows:	Numbers and corresponding preparation steps are as follows:	Numbers and corresponding procedures are as follows:		Organic analyses on conc samples will be coded as follows:	Resulting LC fractions for grav./IR/LRMS analyses will be numbered in order, 1-7
			Organic	Inorganic		
100-199, TRW West Coast 200-299, TRW East Coast 300-399, GCA	1-bulk liquid (separated from a slurry) 2-bulk liquid (separated from a slurry) 3-bulk liquid 4-bulk liquid FF-liquid fuel feed CD-condensate from XAD-2 module PR-solvent probe/ cyclone rinse MR-solvent XAD-2 module rinse HM-HNO_3 XAD-2 module rinse HI-H202 impinger AI-APS impingers XR-XAD-2 resin PF-filter(s) 1C-1-3μ cyclone 3C-3-10μ cyclone 10C->10μ cyclone XM-XR extract plus MR CH-HM plus CD plus HI FC-PF plus 1C CC-3C plus 10C CF-solid fuel feed (coal) 5-bulk solids 6-bulk solids 7-bulk solids (separated from a slurry) 8-bulk solids (separated from a slurry)	0-no preparation LE-liquid-liquid extraction SE-Soxhlet extraction A-acidified aliquot B-basified aliquot PB-Parr bomb combustion HW-hot water extraction AR-aqua regia extraction	0-no conc required GC-C_7-C_{17} GC KD-K-D Conc	SS-SSMS AAS-Hg,As,Sb SO_4-SO_4 NO_3-NO_3 CF-Cl,F	GM-GC/MS for PAHs GI-Grav.,IR MS-LRMS LC-LC separation	

Figure 4-4. EACCS Sample Control Numbers

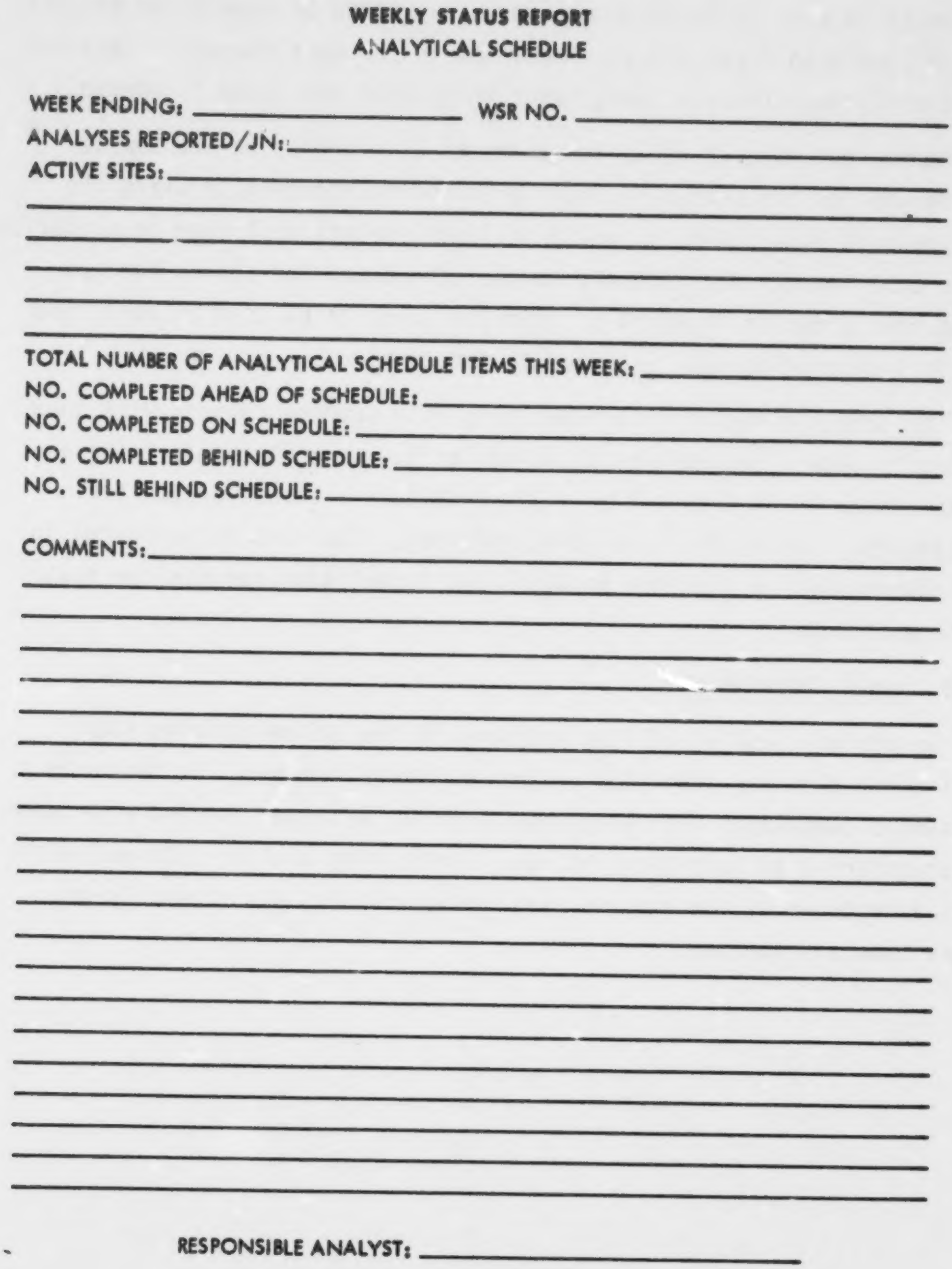
worksheets is kept by the bank manager as a record of samples in process and the completed forms are also returned to the bank manager. Examples of the analytical traveler worksheets to be used are shown in Appendix B.

At the end of each week, the analysts will report to the Sample Bank Manager on the status of their areas of responsibility using the form shown in Figure 4-5. These individual reports will then be summarized by the bank manager and reported to the Laboratory Operations Manager on the form shown in Figure 4-6. Similar forms to be used at month end will include cost as well as schedule information.

The schedule data provided on the weekly summary reports will then be used to update the analytical schedule flow control charts. These charts, shown in Figures 4-7 to 4-9, constitute a visual system for tracking the status of all on-going analyses. They are to be posted in the laboratories so that the analysts and technicians can monitor their sample workload.

4.1.6 Sample Retainment

In-process samples will be retained in the active storage areas until completion and submittal of the analytical report. At that time, the sample containers will be purged with dry nitrogen, sealed with tape, and transferred to long-term storage. There they will be retained until EPA's acceptance of the reports pertaining to them, but generally not longer than six months.



WEEKLY STATUS REPORT
ANALYTICAL SCHEDULE

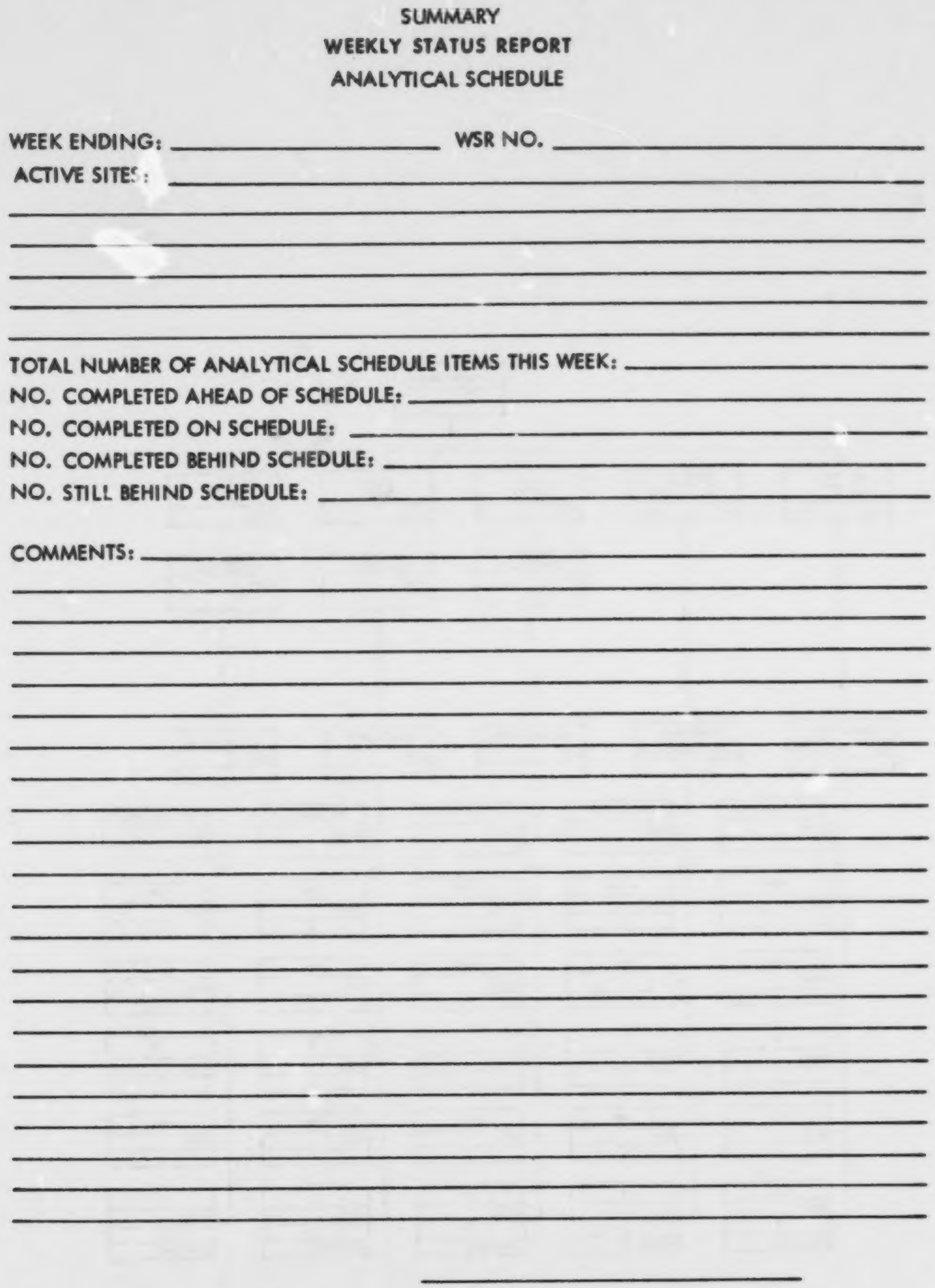
WEEK ENDING: ____________ WSR NO. ____________
ANALYSES REPORTED/JN: ____________
ACTIVE SITES: ____________

TOTAL NUMBER OF ANALYTICAL SCHEDULE ITEMS THIS WEEK: ____________
NO. COMPLETED AHEAD OF SCHEDULE: ____________
NO. COMPLETED ON SCHEDULE: ____________
NO. COMPLETED BEHIND SCHEDULE: ____________
NO. STILL BEHIND SCHEDULE: ____________

COMMENTS: ____________

RESPONSIBLE ANALYST: ____________

Figure 4-5. Weekly Status Report



SUMMARY
WEEKLY STATUS REPORT
ANALYTICAL SCHEDULE

WEEK ENDING: ____________________ WSR NO. ____________________

ACTIVE SITES: ____________________

TOTAL NUMBER OF ANALYTICAL SCHEDULE ITEMS THIS WEEK: ____________

NO. COMPLETED AHEAD OF SCHEDULE: ____________

NO. COMPLETED ON SCHEDULE: ____________

NO. COMPLETED BEHIND SCHEDULE: ____________

NO. STILL BEHIND SCHEDULE: ____________

COMMENTS: ____________________

Figure 4-6. Summary: Weekly Status Report

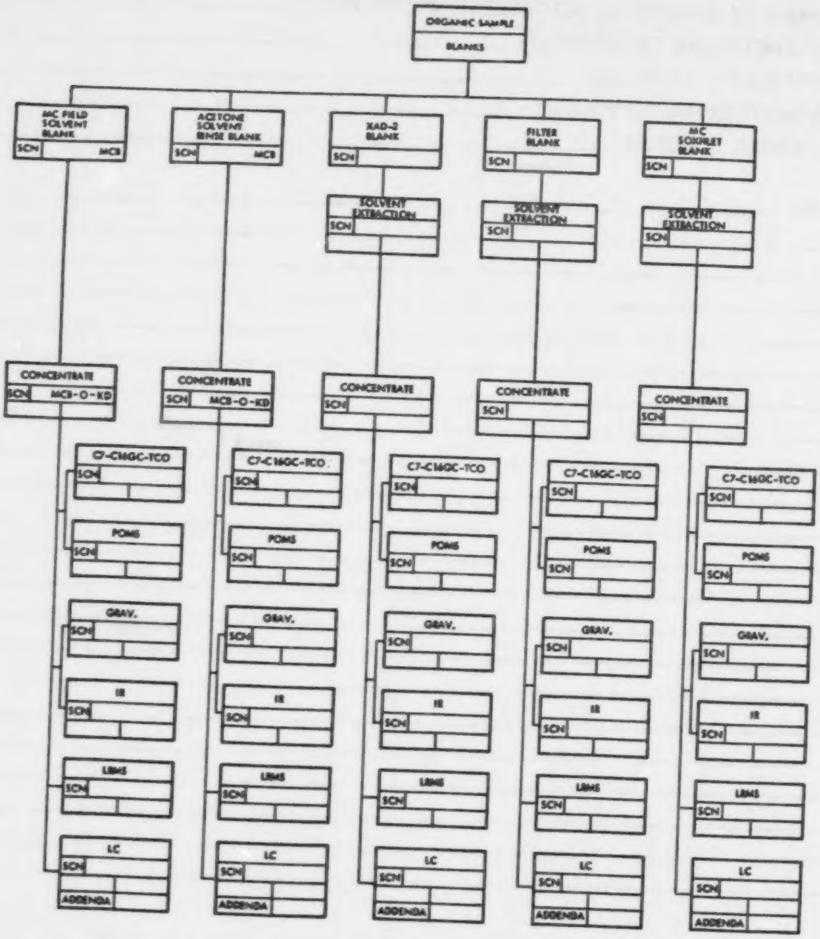
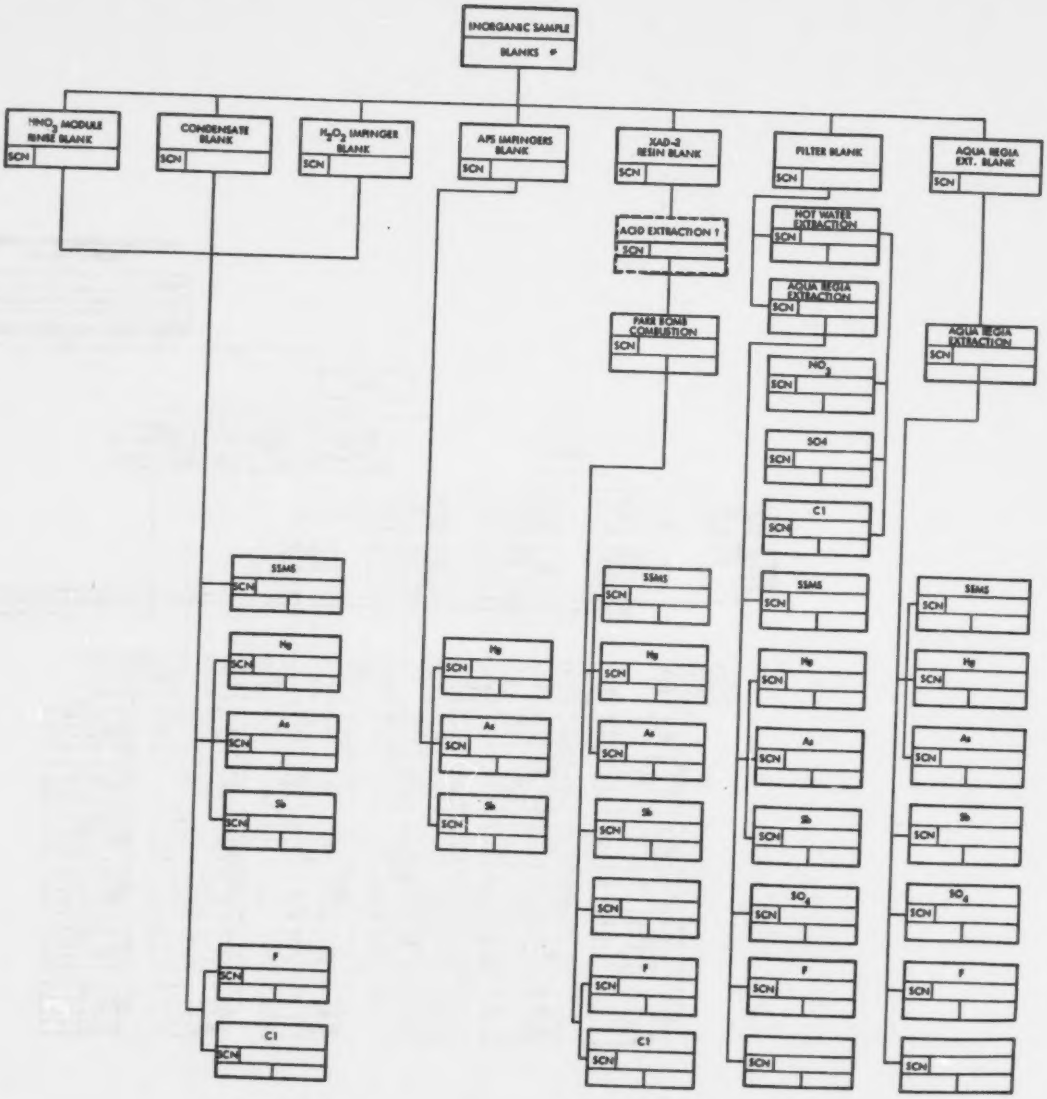

ORGANIC SAMPLE
BLANKS
MC FIELD SOLVENT BLANK
SCN
MCB
ACETONE SOLVENT RINSE BLANK
SCN
MCB
XAD-2 BLANK
SCN
FILTER BLANK
SCN
MC SOXHLET BLANK
SCN
SOLVENT EXTRACTION
SCN
SOLVENT EXTRACTION
SCN
SOLVENT EXTRACTION
SCN
CONCENTRATE
SCN
MCB-O-KD
CONCENTRATE
SCN
MCB-O-KD
CONCENTRATE
SCN
CONCENTRATE
SCN
CONCENTRATE
SCN
C7-C16GC-TCO
SCN
POMS
SCN
GRAV.
SCN
IR
SCN
LRMS
SCN
LC
SCN
ADDENDA

Figure 4-7. Analytical Schedule Flow Control Chart (Sht 1 of 2--Organic)


INORGANIC SAMPLE
BLANKS *
HNO$_3$ MODULE RINSE BLANK
SCN
CONDENSATE BLANK
SCN
H$_2$O$_2$ IMPINGER BLANK
SCN
APS IMPINGERS BLANK
SCN
XAD-2 RESIN BLANK
SCN
FILTER BLANK
SCN
AQUA REGIA EXT. BLANK
SCN
ACID EXTRACTION †
SCN
PARR BOMB COMBUSTION
SCN
HOT WATER EXTRACTION
SCN
AQUA REGIA EXTRACTION
SCN
AQUA REGIA EXTRACTION
SCN
NO$_3$
SO4
Cl
SSMS
Hg
As
Sb
SO$_4$
F
Cl
SCN

* AFTER 8/1/78, ALL As, Sb, Cl AND F ANALYSIS ARE ON AN OPTIONAL BASIS

† PROPOSED - SEE SECTION 8.2

Figure 4-7. Analytical Schedule Flow Control Chart (Sht 2 of 2--Inorganic)

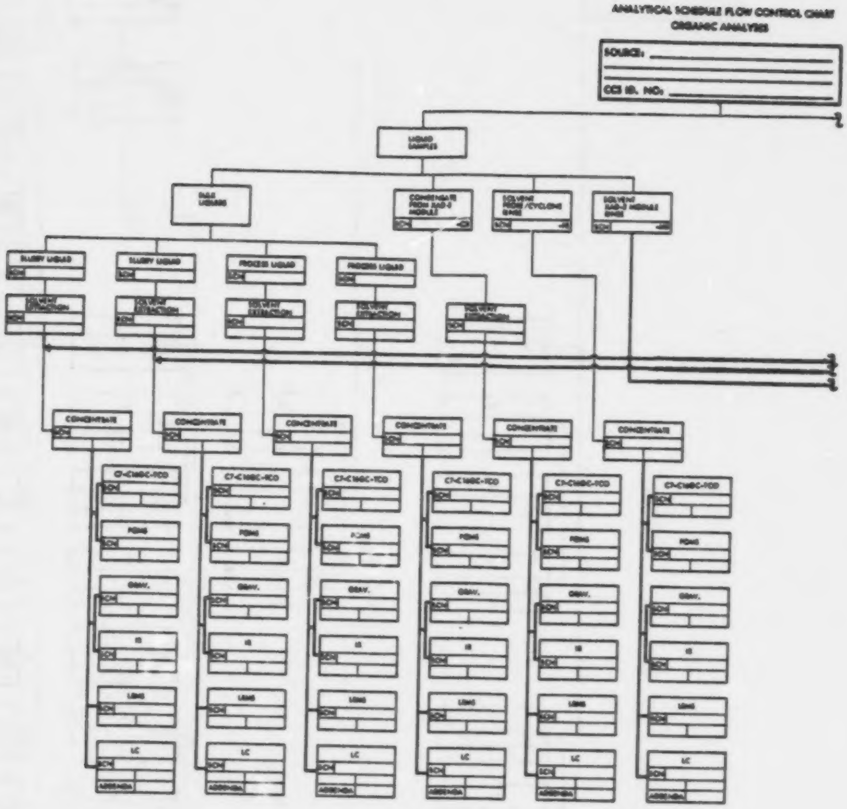

ANALYTICAL SCHEDULE FLOW CONTROL CHART
ORGANIC ANALYSES
SOURCE:
CCI ID. NO:
LIQUID SAMPLES
BULK LIQUIDS
CONDENSATE FROM XAD-2 MODULE
SOLVENT FROM /CYCLONE RINSE
SOLVENT XAD-2 MODULE RINSE
SLURRY LIQUID
SLURRY LIQUID
PROCESS LIQUID
PROCESS LIQUID
SOLVENT EXTRACTION
CONCENTRATE
C7-C16GC-TCO
GRAV.
IR
LRMS
LC
ADDENDA

Figure 4-8. Analytical Schedule Flow Control Chart (Sht 1 of 2) (Liquid/Organic Analysis)

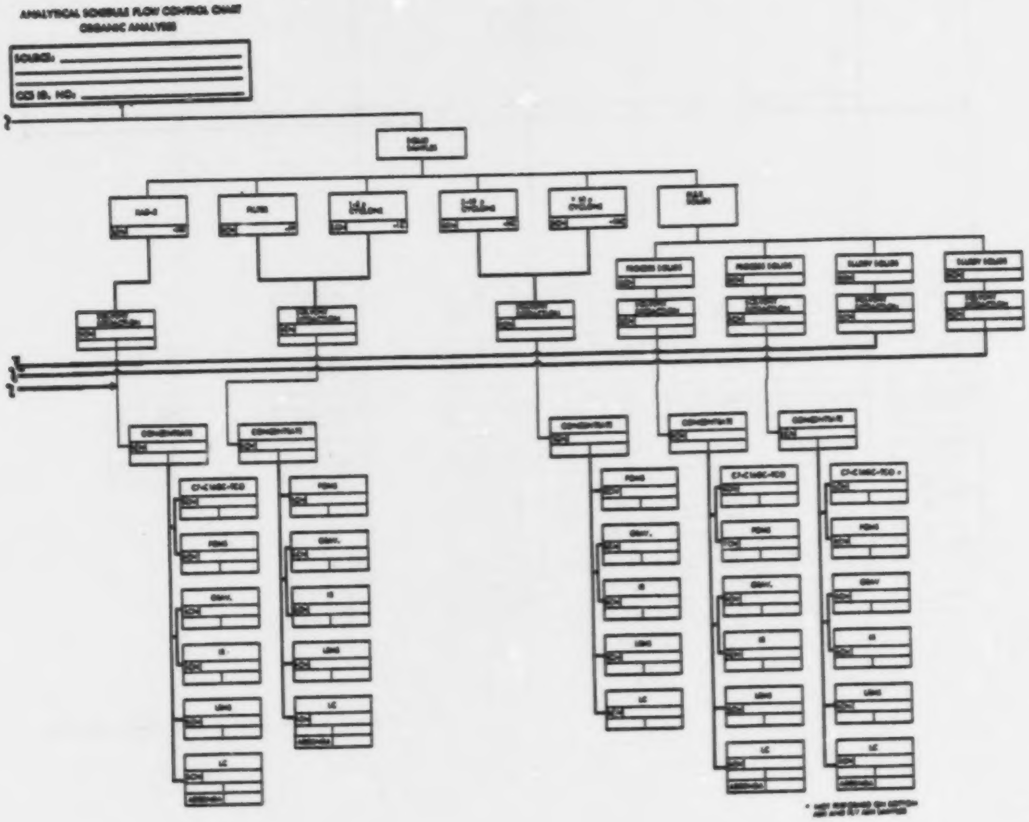

ANALYTICAL SCHEDULE FLOW CONTROL CHART
ORGANIC ANALYSIS
SOURCE:
CCS ID. NO:
CONCENTRATE
GRAV.
IR
LC

Figure 4-8. Analytical Schedule Flow Control Chart (Sht 2 of 2)
(Solid/Organic Analysis)

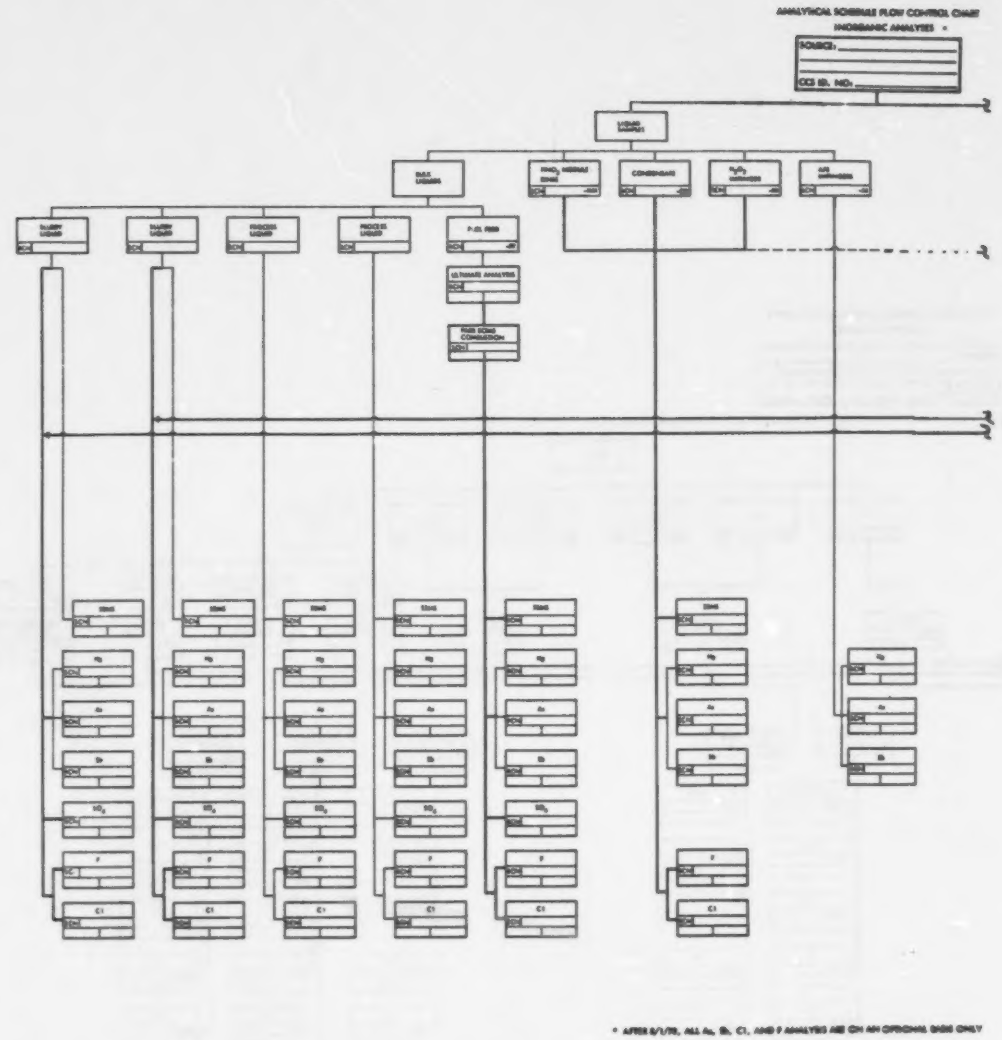
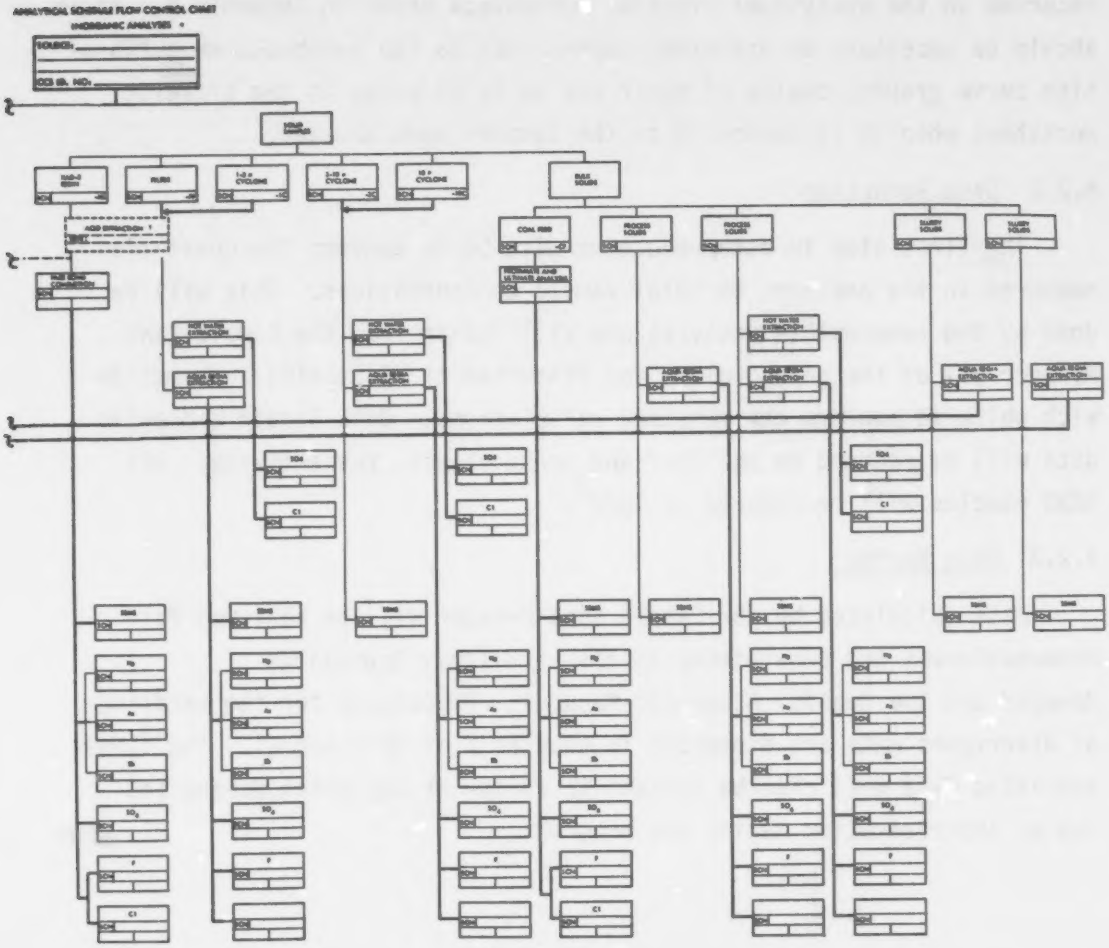

ANALYTICAL SCHEDULE FLOW CONTROL CHART
INORGANIC ANALYSES *
SOURCE:
CCS ID. NO:
LIQUID SAMPLES
BULK LIQUIDS
CONDENSATE
SLURRY LIQUID
PROCESS LIQUID
ULTIMATE ANALYSIS
SCN
Hg
As
Sb
SO4
F
Cl

Figure 4-9. Analytical Schedule Flow Control Chart (Sht 1 of 2) (Liquid/Inorganic Analysis)


ANALYTICAL SCHEDULE FLOW CONTROL CHART
INORGANIC ANALYSES *
SOURCE:
CCS ID. NO.:
SOLID SAMPLES
FILTER
1-3 μ CYCLONE
3-10 μ CYCLONE
10 μ CYCLONE
BULK SOLIDS
ACID EXTRACTION †
COAL FEED
PROCESS SOLIDS
PROCESS SOLIDS
SLURRY SOLIDS
SLURRY SOLIDS
PROXIMATE AND ULTIMATE ANALYSIS
HOT WATER EXTRACTION
AQUA REGIA EXTRACTION
SO4
Cl
Hg
As
Sb
SO4
F
Cl

* AFTER 8/1/78, ALL As, Sb, Cl, AND F ANALYSES ARE ON AN OPTIONAL BASIS ONLY

† PROPOSED - SEE SECTION 8.2

Figure 4-9. Analytical Schedule Flow Control Chart (Sht 2 of 2)
(Solid/Inorganic Analysis)

4.2 DATA MANAGEMENT

4.2.1 Data Recording

All primary data generated by the analysts and technicians will be recorded on the analytical traveler worksheets shown in Appendix B. If it should be necessary to use other papers such as lab notebooks or calibration curve graphs, copies of these are to be attached to the traveler worksheet when it is turned in to the Sampler Bank Manager.

4.2.2 Data Reduction

The first step in data reduction will be to convert the quantities measured in the analyses to total sample concentrations. This will be done by the responsible analysts who will obtain from the Sample Bank Manager all of the gross volume and disbursement aliquoting information with which to perform the required calculations. Bulk liquid and solid data will be reduced to mg/liter and mg/kg values, respectively. All SASS samples will be reduced to mg/m^3.

4.2.3 Data Review

Data calculated by the Sample Bank Manager will be reviewed for reasonableness and consistency by the Laboratory Operations Manager and the Quality Assurance Manager. Procedures for the handling of discrepant data are discussed in Chapter 2 of this manual. The final tabulated data will also be subject to review at any point during its use or interpretation during the program.

5.0 FIELD SAMPLING

5.1 INTRODUCTION

This chapter covers the sampling methodology to be used during the field effort to collect the required samples for analysis. The methods are as detailed as possible, but it should be realized that every detail for every source cannot be covered. It is important therefore, that the personnel involved in the field effort be well trained and experienced. Accurate records and notes must be maintained to document specific operations carried out at each location. Sound engineering judgment must be exercised. In those unusual circumstances that warrant, the field team will contact the project manager to resolve a specific problem, thus relying on a single source for these decisions throughout the program. This will help to provide continuity and uniformity.

5.2 SAMPLING IN PARTICULATE LADEN STREAMS

5.2.1 Scope and Application

This method will be used on those sources having a ducted effluent from combustion sources.

5.2.2 Summary of Method

The method extracts a sample from the gas stream through a sample nozzle at a rate approximately equal to the flue gas velocity. The particulate matter is collected by a series of cyclones and a filter, and then the gaseous constituents are collected by an adsorbent module and absorbing solutions. Provisions are made to monitor all the required parameters such as temperatures, pressures, and volumes. The sample fractions are then recovered and shipped to the laboratory for analysis.

5.2.3 Definitions

SASS - Source Assessment Sampling System

SSMS - Spark Source Mass Spectometry

V/V - Volume to Volume

5.2.4 Apparatus: The SASS Train

The sampling train to be used for gaseous streams containing particulate matter consists of a stainless steel probe which enters an oven module containing 3 cyclones and a filter. Size fractionation is accomplished in the series cyclone portion of the SASS train, which incorporates the cyclones in series to provide large quantities of particulate matter size-classified into three ranges: a) ≥10 μm, b) 3 μm to 10 μm, and c) 1 μm to 3 μm. Together with a 142 mm filter a fourth cut, <1 μm, is obtained. Volatile organic material is collected in a XAD-2 sorbent trap. The XAD-2 trap is an integral part of the gas treatment system which follows the oven containing the cyclone system (See Figure 5-1). The gas treatment system is composed of four primary components: the gas conditioner, the XAD-2 adsorbent trap, the aqueous

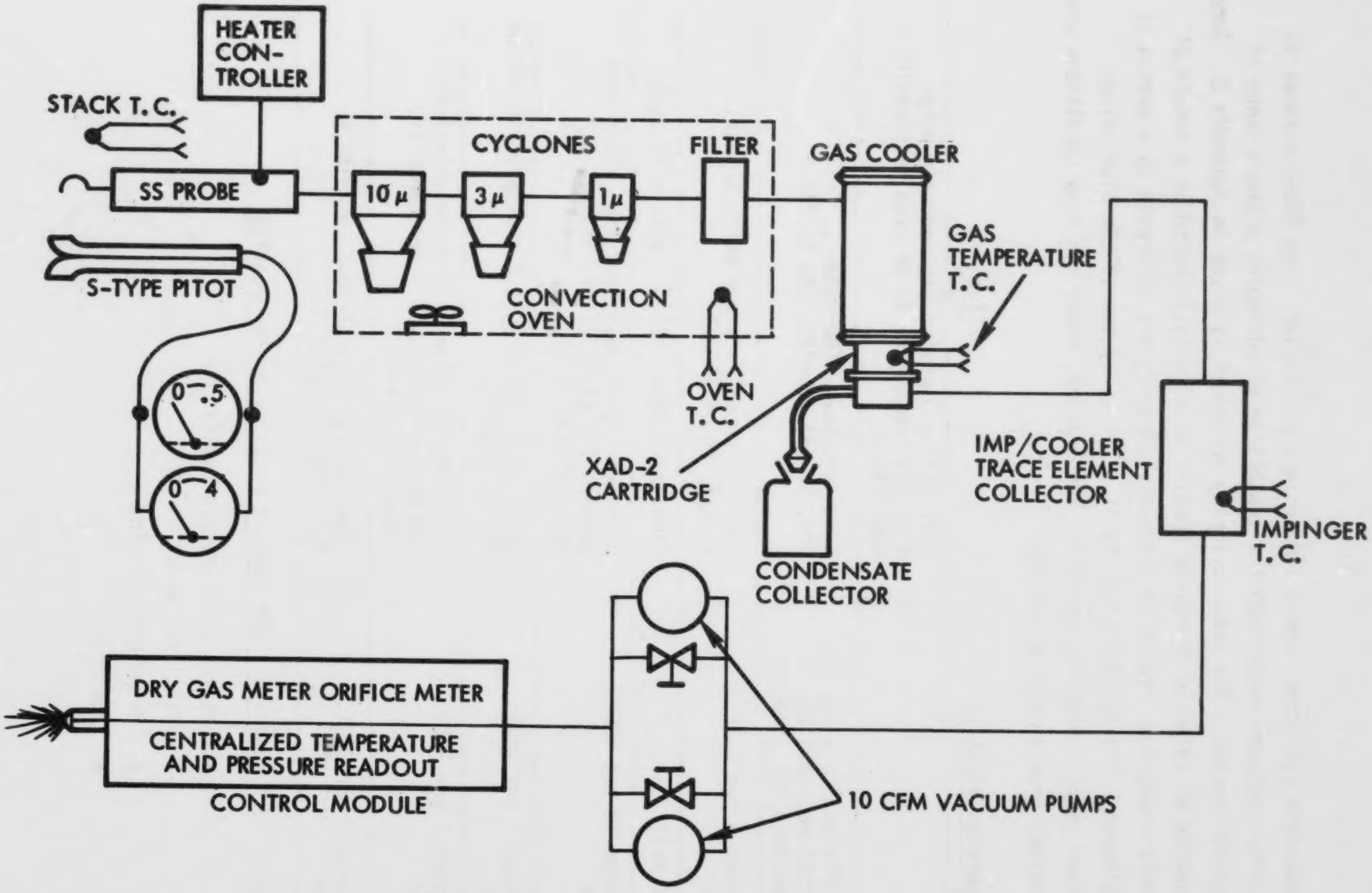

HEATER CON- TROLLER
STACK T.C.
SS PROBE
S-TYPE PITOT
0 .5
0 4
CYCLONES
10 μ
3 μ
1 μ
FILTER
CONVECTION OVEN
OVEN T.C.
GAS COOLER
GAS TEMPERATURE T.C.
XAD-2 CARTRIDGE
CONDENSATE COLLECTOR
IMP/COOLER TRACE ELEMENT COLLECTOR
IMPINGER T.C.
10 CFM VACUUM PUMPS
DRY GAS METER ORIFICE METER
CENTRALIZED TEMPERATURE AND PRESSURE READOUT
CONTROL MODULE

Figure 5-1. SASS Schematic

condensate collector, and a temperature controller. The XAD-2 sorbent is a porous polymer resin with the capability of adsorbing a broad range of organic species. The resin cleaning procedure is given in Appendix E. Some trapping of volatile inorganic species is also anticipated as a result of simple impaction. Volatile inorganic elements are collected in a series of impingers. The pumping capacity is supplied by two 10-cfm high volume vacuum pumps. Required pressure, temperature, power and flow conditions are obtained from a main controller.

Apparatus Quantity	Item
3	Five-gallon glass or high density polyethylene containers to be used in cleaning operations.
Sufficient to allow for rotational mailings to home base for cleaning	Nylon brushes - TRW Material Cat. Nos. SB-941, BS-942, and BS-943.
Assume 3 per SASS run	150 x 15 mm polystyrene petri dishes, SP Cat. No. D1990-25
One roll	Clean-room grade nylon 1 yard x 20 yards
Assume 10 per SASS run	High density polyethylene wide mouth containers for particulate, Thomas No. 1720-Q33 (6 oz.)
Assume 5 per SASS run	Amber glass containers for organic solutions 500 ml capacity
Assume 5 per SASS run	High density polyethylene containers for impinger solutions, 1 liter capacity, Thomas No. 1706-K73
Assume 2 per SASS run	High density polyethylene containers 0.5 liter capacity.

5.2.5 Reagents: ACS Reagent Grade or Better Quality

- Nitric acid (concentrated)
- Distilled water
- Methylene chloride
- Acetone

- Silica gel desiccant - (3-8 mesh)
- Hydrogen peroxide - 30%
- Silver nitrate
- Ammonium persulfate

5.2.6 Sample Collection

The following sections discuss the equipment preparation required for the SASS train, including cleaning procedures of the train components and sample containers, and apparatus checkout. The SASS train schematic and other parts of the train are shown in Figure 5-1.

Precleaning Procedures for the SASS Train and Sample Containers

The SASS train is the most complex sampling unit discussed in this manual, and an overall generalized cleaning procedure cannot be established. Two primary cleaning methodologies are required. The first methodology described in this section concerns the technique involved in producing biologically inert surfaces throughout the SASS train. The second methodology presents the techniques required for cleaning or removing sample from various parts of the train after the run (Section 5.2.11). All cleaning procedures are shown diagrammatically in Figure 5-2.

The first stage in preparing the sampling train and sample containers for sample collection is prepassivation with a nitric acid solution. All surfaces in the sampling train which come in contact with sample, as well as all sample containers and containers for the impingers, will be prepassivated by a 60-minute standing contact with 15% (V/V) aqueous nitric acid. Agitate the parts initially to remove trapped air bubbles. Rinse in a second solution of 15 percent (V/V) HNO_3 by dipping and agitating the part in the solution for approximately 10 seconds. Remove HNO_3 by rinsing with distilled water. Re-rinse by spraying thoroughly with acetone, covering all surfaces of the part, or dip in acetone and agitate for 10 seconds. Blow dry with purified air.

Note that acetone has been substituted for isopropyl alcohol.

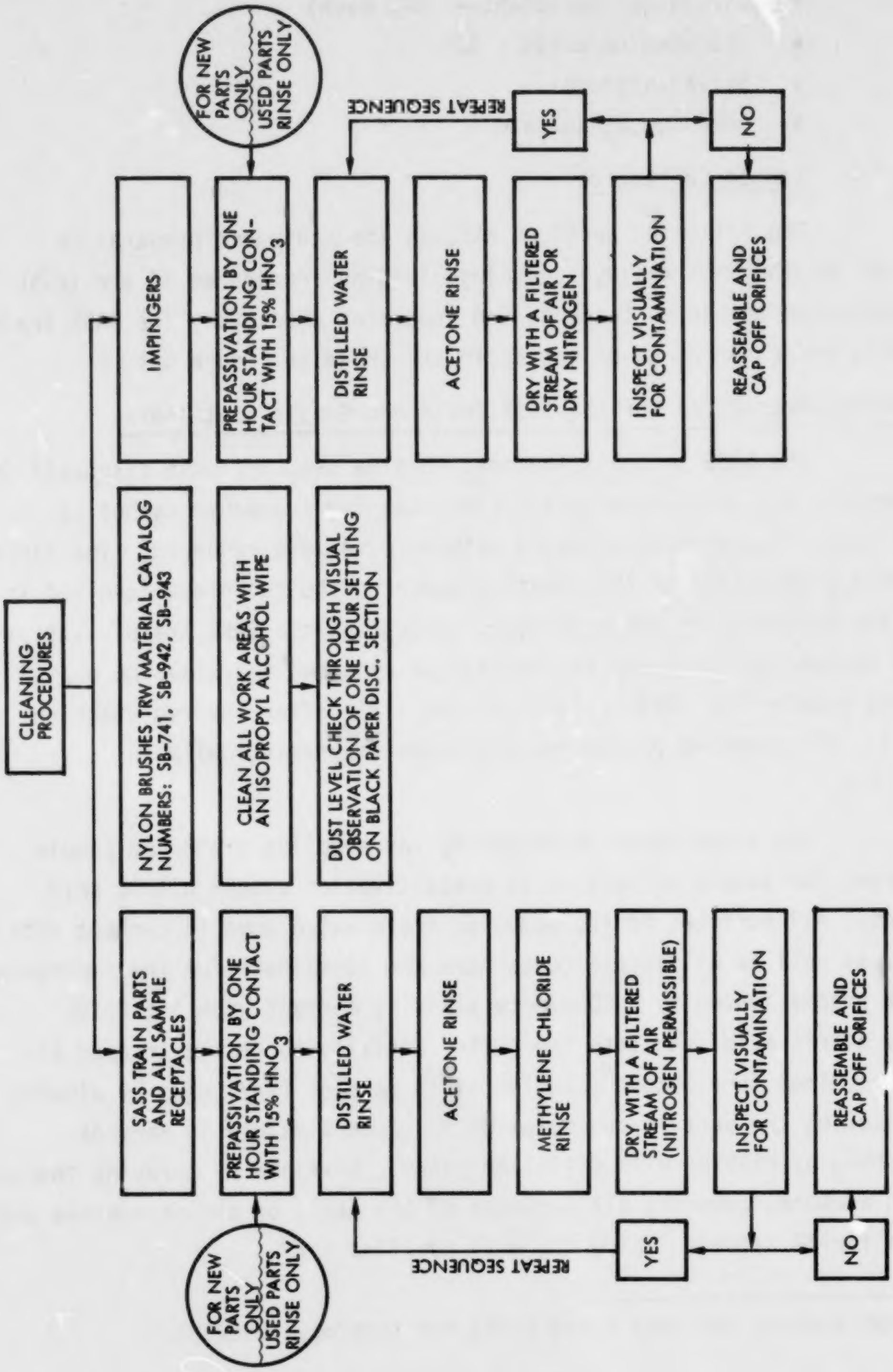

CLEANING PROCEDURES
SASS TRAIN PARTS AND ALL SAMPLE RECEPTACLES
PREPASSIVATION BY ONE HOUR STANDING CONTACT WITH 15% HNO3
DISTILLED WATER RINSE
ACETONE RINSE
METHYLENE CHLORIDE RINSE
DRY WITH A FILTERED STREAM OF AIR (NITROGEN PERMISSIBLE)
INSPECT VISUALLY FOR CONTAMINATION
REASSEMBLE AND CAP OFF ORIFICES
YES
NO
REPEAT SEQUENCE
FOR NEW PARTS ONLY
USED PARTS RINSE ONLY
NYLON BRUSHES TRW MATERIAL CATALOG NUMBERS: SB-741, SB-942, SB-943
CLEAN ALL WORK AREAS WITH AN ISOPROPYL ALCOHOL WIPE
DUST LEVEL CHECK THROUGH VISUAL OBSERVATION OF ONE HOUR SETTLING ON BLACK PAPER DISC, SECTION
IMPINGERS
PREPASSIVATION BY ONE HOUR STANDING CONTACT WITH 15% HNO3
DISTILLED WATER RINSE
ACETONE RINSE
DRY WITH A FILTERED STREAM OF AIR OR DRY NITROGEN
INSPECT VISUALLY FOR CONTAMINATION
REASSEMBLE AND CAP OFF ORIFICES
YES
NO
REPEAT SEQUENCE
FOR NEW PARTS ONLY
USED PARTS RINSE ONLY

Figure 5-2. SASS Cleaning Procedures

Passivation should be carried out every six months when the frequency of tests is one per month or less, every three months when the frequency of tests is between one per week and one per month, and monthly for testing in excess of one per week. If the tests are more frequent or of longer duration, passivation should be conducted more frequently. If corrosion has occurred, the corrosion should be removed and the passivation repeated.

The passivation and rinse solutions should be replaced after every fourth use and should be discarded weekly.

Two separate approaches are used for subsequent cleanings, one for SASS train components and organic sample receptacles, and the other for bottles holding impinger solutions. The first group is cleaned in three successive stages using a different solvent in each stage. The solvents used are distilled water, acetone, and methylene chloride, in the order listed. ACS reagent grade shall be used. Two washings with each solvent will be accomplished. This procedure removes all extraneous particulate matter and produces a clean, dry surface. As each part is treated with the final solvent (methylene chloride), it is purged dry in a filtered stream of air or dry nitrogen and visually inspected thoroughly for any sign of contaminating residue, scale, rust, etc. A contaminated train component may not be used in a sampling run. All equipment treated in the above fashion must be placed in a clean area to await the next test.

The bottles holding the impinger solution are cleaned in two successive stages, involving distilled water, followed by acetone.

The field area in which these cleaning operations are performed must be as clean as possible under existing field conditions. An enclosed space is required in which reasonable precaution has been taken to remove spurious dust, dirt or particulate contaminants. Reasonable precaution is intended to mean that the area has been swept clean; doors or significant draft inducing sources have been closed and; an isopropyl alcohol wipe has been performed over the work bench area. A laminar flow bench will be used for handling the various fractions of the sample during recovery.

To ensure work area cleanliness, dust level checks are run using the following procedure. A disc of black glazed weighing paper (Sargent Welch #S-65225-A) is placed in an open petri dish and allowed to stand on a bench in the work area. Wipe a finger across the paper. If no dust appears to have been brushed off the paper, the area is clean enough to proceed with sample transfer and/or cleaning operations. If a dust trace is visible on the paper, the area must be cleaned and appropriate measures must be taken to lower the dust levels. This may involve dusting and sweeping the area, performing counter wipes, etc. A second paper disc is then placed in the work area and the dust level check procedure is repeated until no visible dust trace is observed.

5.2.7 Pre-Test Checkout Operations

Prior to test-site arrival a number of checkpoints are required to ensure a smooth field operation.

1) Sufficient quantity of solvents are required to maintain adequate reserves during the elapsed time in the field.

2) A tank of purified dry nitrogen or a clean compressed air source must be available in the van.

3) Swagelok fittings for each SASS train must be on inventory in triplicate.

4) All SASS train parts must be closely examined for defects which might induce down time problems in the field.

5) The entire system must be leak checked.

The SASS train leak checking procedure is described in detail in the operator's manual. Briefly, the procedure involves assembling the entire train, sealing off the probe tip, bringing the oven and probe to operating temperatures, turning on the pump and observing flow meter gauges for the existence of any appreciable flow. The allowable SASS train leak rate for a Level 1 test is 0.05 cfm at 20 inches of Hg. If an unacceptable leak rate is found, move in the direction of the probe starting at the pump and tighten each fitting in order to ensure that a loose fitting is not responsible for the problem. If this action does not solve the leak problem, the train must be disassembled on a modular basis starting at the pump and progressing towards the probe while leak-checking each individual module until the problem area is pinpointed. Once discovered, if the problem is one which cannot be solved with the materials at hand, it is to be designated as the manufacturer's responsibility and substitute spare parts should be obtained. Under no condition may a sampling test be conducted with a leak rate in excess of 0.05 cfm at 20 inches of Hg.

5.2.8 SASS Train Cyclone Deletion Guidelines

Due to the lower grain loadings encountered in many oil and gas fired boilers, a set of decision criteria has been developed for cyclone deletion in order to maximize the amount of useful data obtained. The nomograph presented in Figure 5-3 illustrates the estimated $>3\mu$ and $<3\mu$ catches as a function of grain loading. (Use of Figure 5-3 is described in Chapter 3.) Based on this figure decisions may be made to retain or remove the 1, 3, and/or 10 micron cyclones as indicated in Table 5-1. In general, a projected catch of 5-10 mg in a given cyclone results in that cyclone being eliminated. This cutoff point was chosen because samples of this size represent the lower limit of recovery and are only marginal in terms of analysis (i.e., only SSMS can be performed). Table 5-1 will be used, subject to the following criteria:

- The maximum expected grain loading will be determined using previous test data or estimates provided by site personnel, actual TRW field experience, and existing data concerning similar sites. When in doubt, the next higher grain loading will be used.
- All catches will be photomicrographed, examined visually for significant quantities of oversize particulate, and a rough particle size distribution will be determined.
- If the field test produces results that indicate the use of additional cyclones, the test will be repeated.
- Additional cyclones will be used if special conditions indicate.

Table 5-2 shows how the decision criteria are expected to apply to the combustion source categories to be tested in this program. In all cases, the conservative approach will be taken and an additional cyclone will be used for the first 1 or 2 sites tested using each type of fuel.

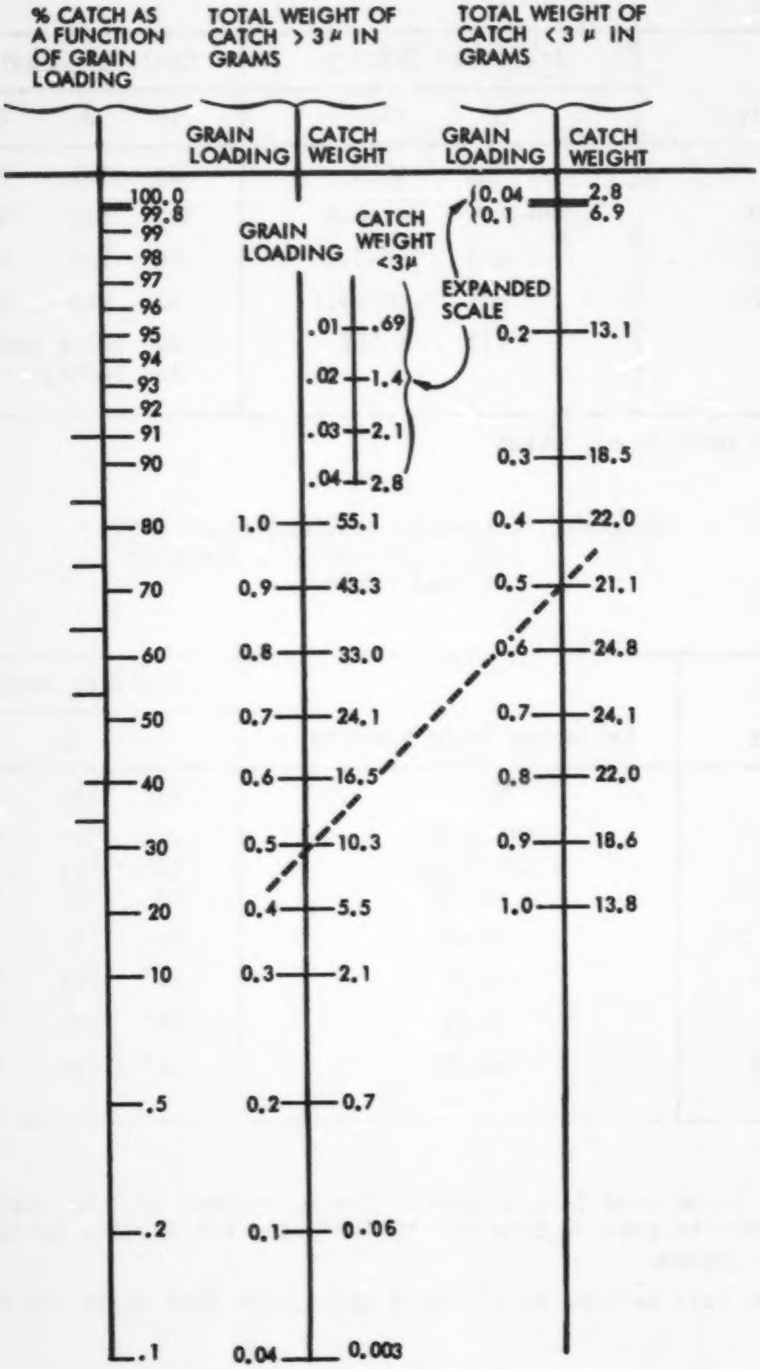


Figure 5-3. Particulate Analysis Prediction Nomograph

Table 5-1. SASS Train Cyclone Use Criteria*

Grain Loading	Projected Catch g		Cyclones Required†		
	>3μ	<3μ	1μ	3μ	10μ
>0.11	>.006	>6.9	Yes	Yes	Yes
0.051-0.10	.004-.006	3.1-6.9	Yes	Yes	No
0.021-0.050	nil	1.4-3.1	No	Yes	No
0.0001-0.020	nil	0.007-1.4	No	Yes	No
<0.0001	nil	<.007	Run XAD-2 module and impingers only		

*A filter is used in all cases.

Table 5-2. Expected Application of SASS Train Cyclone as a Function of Fuel Type*

Fuel Type	Projected Grain Loading	Cyclones Required†		
		1μ	3μ	10μ
Coal	>0.1	Yes	Yes	Yes
Residual Oil	0.051-0.10	Yes	Yes	No
	0.021-0.05	Yes	Yes	No
	<0.020	No	Yes	No
Distillate Oil	<0.02	No	Yes	No
Natural Gas	<0.02	No†	Yes	No
Gasoline	<0.02	No†	Yes	No
Diesel Fuel	<0.02	No†	Yes	No

*A filter is to be used in all cases. The 3μ cyclone will be used in all tests in order to provide data for the EPA Fine Particulate Emissions Information System.

†This cyclone will be used until field tests show that it is not necessary.

5.2.9 Sample Acquisition

This section is divided into two predominant parts: the first part lists briefly the specific steps required to obtain a sample, while the second part describes in detail the procedures required in performing each step. In this way, personnel familiar with the functional requirements of each step are not hindered by unnecessary narrative, while those who are not familiar with certain aspects of the operation may refer to the second part of this section.

Assuming that all SASS train components and sample receptacles have been treated and cleaned in accordance with the foregoing procedures, a Level 1 sample will be taken as follows.

5.2.9.1 Sample Acquisition Steps

1) Fill the impinger bottles with the reagents and volumes specified in Table 5-3.

2) Assemble sampling apparatus in accordance with the manufacturer's specifications.

3) Preheat the probe and the oven. Under most conditions, 15 to 30 minutes are required for these components to reach operating temperature. The oven and probe shall be maintained at 205°C (400°F). For gas fired units the oven and probe temperature shall be maintained at 150°C (300°F).

4) Measure the stack temperature, moisture content, and velocity profile. Determine the position in the stack which corresponds to the average stack velocity (See Section 5.2.9.2).

5) Leak test the system. The allowable leak rate for a Level 1 test is 0.05 cfm at 20 inches of mercury. Leak rates in excess of this value must be corrected.

6) Using the procedures and calibration curves supplied by the manufacturer, compute the appropriate sampler flow rate and the proper nozzle size.

7) Install the nozzle on the probe, and then insert the probe into the stack or duct. The nozzle should be in the proper position in the duct, as determined in step 4.

Table 5-3. SASS Train Impinger System Reagents

Impinger	Reagent	Quantity	Purpose
#1	30% H_2O_2(a,b)	500 ml	Trap reducing gases such as SO_2 to prevent depletion of oxidative capability of trace element collecting impingers 2 and 3.
#2	0.2 M $(NH_4)_2S_2O_8$(b) +0.02 M $AgNO_3$	500 ml	Collection of volatile trace elements by oxidative dissolution.
#3	0.2 M $(NH_4)_2S_2O_8$(b) +0.02 M $AgNO_3$	500 ml	Collection of volatile trace elements by oxidative dissolution.
#4	Silica Gel (color indicating)	900 g	Prevent moisture from reaching pumps and used for moisture calculations.

a. Variable depending on SO_2 content.

b. All solutions prepared fresh daily.

8) To initiate the sampling run, turn on the vacuum pump and throttle the intake valve to achieve the flow rate determined (in step 6).

9) During the course of the run, minimum of 20-minute checks and adjustment of flow rates and temperatures will be made and recorded on a standard data sheet.

5.2.9.2 Procedural Details for Individual Steps

The nine previously listed sample acquisition steps are self-explanatory for step numbers 1, 3, 7, 8 and 9. Numbers 2, 4, 5 and 6 require additional elaboration for indivuduals unfamiliar with these applications.

- Step 2, Apparatus Assembly

  The appropriate procedures to be used are detailed in the Aerotherm operating manuals.

- Step 4, Temperature, Moisture and Velocity Profile

  The general framework from standard EPA methods 1 through 4 will be used to determine the stack gas velocity profile. Since EPA standard methods 1 through 4 are compliance methods they require degrees of accuracy in excess of those needed for Level 1. In Level 1, for example, sophisticated moisture determinations (Method 4) are unnecessary since plant data or stoichiometric calculations will suffice. Also, Orsat analysis (Method 3) to determine stack gas composition is unnecessary since GC data will exist for this purpose. The mathematics used in determining the velocity profile are independent of the data acquisition technique and will therefore be used as stipulated in the standard methods. Modified versions of Methods 1 and 2 which are appropriate for Level 1 sampling are explained in detail in sections 5.2.9.3 and 5.2.9.4.

- Step 5, Leak Test

  The appropriate procedures to be used are detailed in the Aerotherm operating manuals.

- Step 6, Nozzle and Flow Rate Selection

  The appropriate procedures to be used are detailed in the Aerotherm operating manuals.

5.2.9.3 Method 1 - Sample and Velocity Traverses for Stationary Sources

1) Principle and applicability

A sampling site and the number of traverse points are selected to aid in the extraction of a representative sample. This method is applicable to sampling of gas streams contained in ducts, stacks, or flues.

It is intended that all new sources consider the requirements of this method before construction of the affected facility. Should they be overlooked, some sites may not lend themselves to this method and temporary alterations to the stack or deviation from the standard procedure may be required.

This method is not applicable to stacks containing cyclonic or swirling flow or stacks smaller than about 0.3 m (1 ft) in diameter or 0.07 m^2 (0.8 ft^2) in cross sectional area.

2) Procedure

a) Sampling Site.

Select a sampling site that is at least 8 stack or duct diameters downstream and 2 diameters upstream from any flow disturbance such as a bend, expansion, contraction or visible flame. If impractical, select an alternate site that is at least 2 stack or duct diameters downstream and 0.5 diameter upstream from the flow disturbances. For a rectangular cross section, use an equivalent diameter calculated from the following equation to determine the respective distances:

$$D_{\cdot} = \frac{2LW}{L + W} \qquad \text{Equation 5-1}$$

where:

D. = equivalent diameter
L = length
W = width

b) Minimum Number of Traverse Points

When the 8 and 2 diameter criterion can be met, the minimum number of traverse points shall be 12 for stack diameters greater than 0.6 m (24 in.) and 8 for stack diameters equal to or less than 0.6 m (24 in.).

When the 8 and 2 diameter criterion cannot be met use Figure 5-4 to determine the minimum number of traverse points. To use this figure, first determine the distances from the chosen sampling location to the nearest upstream and downstream disturbances. Divide each distance by the diameter or equivalent diameter to determine the distance in terms of the number of duct diameters. Then, determine from Table 5-4 the minimum number of traverse points that corresponds: 1) to the number of duct diameters upstream, and 2) to the number of diameters downstream. Select the higher of the two minimum numbers of traverse points, or a greater value, such that for circular stacks the number is a multiple of four, and for rectangular stacks, the number follows the criteria in section c.

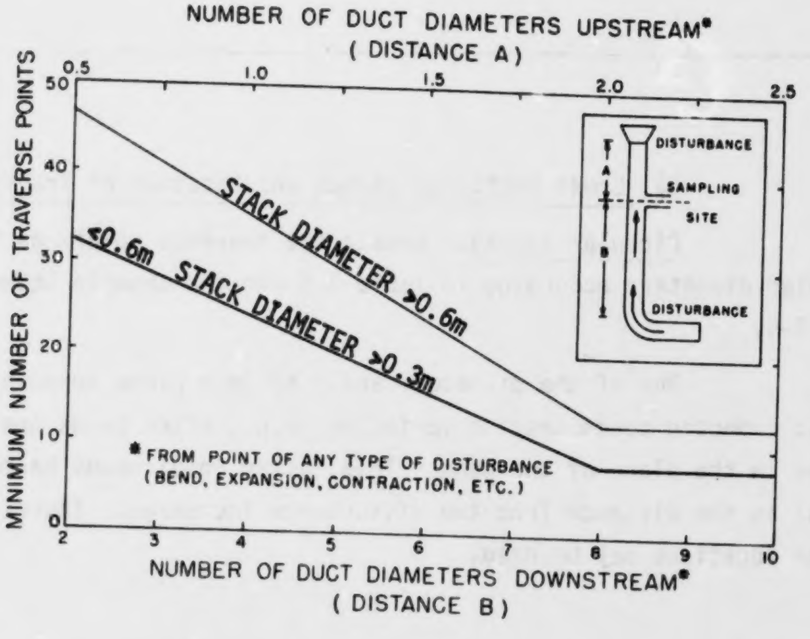


Figure 5-4. Minimum Number of Traverse Points

Table 5-4. Location of Traverse Points in Circular Stacks
(Percent of stack diameter from inside wall to traverse point)

Traverse point number on a diameter	*Number of traverse points on a diameter*											
	2	*4*	*6*	*8*	*10*	*12*	*14*	*16*	*18*	*20*	*22*	*24*
1	14.6	6.7	4.4	3.3	2.5	2.1	1.8	1.6	1.4	1.3	1.1	1.1
2	85.4	25.0	14.7	10.5	8.2	6.7	5.7	4.9	4.4	3.9	3.5	3.2
3		75.0	29.5	19.4	14.6	11.8	9.9	8.5	7.5	6.7	6.0	5.5
4		93.3	70.5	32.3	22.6	17.7	14.6	12.5	10.9	9.7	8.7	7.9
5			85.3	67.7	34.2	25.0	20.1	16.9	14.6	12.9	11.6	10.5
6			95.6	80.6	65.8	35.5	26.9	22.0	18.8	16.5	14.6	13.2
7				89.5	77.4	64.5	36.6	28.3	23.6	20.4	18.0	16.1
8				96.7	85.4	75.0	63.4	37.5	29.6	25.0	21.8	19.4
9					91.8	82.3	73.1	62.5	38.2	30.6	26.1	23.0
10					97.5	88.2	79.9	71.7	61.8	38.8	31.5	27.2
11						93.3	85.4	78.0	70.4	61.2	39.3	32.3
12						97.9	90.1	83.1	76.4	69.4	60.7	39.8
13							94.3	87.5	81.2	75.0	68.5	60.2
14							98.2	91.5	85.4	79.6	73.9	67.7
15								95.1	89.1	83.5	78.2	72.8
16								98.4	92.5	87.1	82.0	77.0
17									95.6	90.3	85.4	80.6
18									98.6	93.3	88.4	83.9
19										96.1	91.3	86.8
20										98.7	94.0	89.5
21											96.5	92.1
22											98.9	94.5
23												96.8
24												98.9

c) Cross Sectional Layout and Location of Traverse Points.

Circular stacks. Locate the traverse points on two perpendicular diameters according to Table 5-4 and the example shown in Figure 5-5.

One of the diameters shall be in a plane containing the greatest expected concentration variation, e.g., after bends one diameter shall be in the plane of the bend. This latter requirement becomes less critical as the distance from the disturbance increases. Therefore, other diameter locations may be used.

TRAVERSE POINT	DISTANCE, % OF DIAMETER
1	4.4
2	14.7
3	29.5
4	70.5
5	85.3
6	95.6

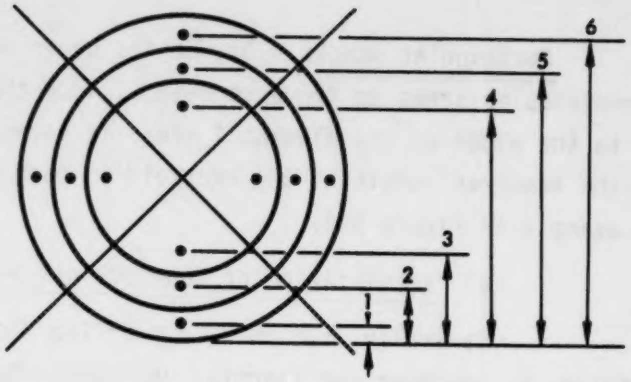


Figure 5-5. Example Showing Circular Stack Cross Section Divided into 12 Equal Areas, with Location of Traverse Points at Centroid of Each Area

In addition, for stacks greater than 0.6 m (24 in.) no sampling points shall be selected within 2.54 cm (1 in.) of the stack walls, and for stacks equal to or less than 0.6 m (24 in.) no sampling points within 1.27 cm (1/2 in.) of the stack walls. To meet these criteria, do the following:

- Stacks greater than 0.6 m (24 in.): When any of the traverse points, as located above, fall within 2.54 cm (1 in.) of the stack walls, relocate them away from the stack walls to a distance of 1) 2.54 cm (1 in.), or 2) a distance equal to the nozzle inside diameter, whichever is larger. These relocated traverse points (on each end of a diameter) shall be the "adjusted" traverse points. In some cases, two successive traverse points may need to be relocated to a single adjusted traverse point at each end of the traverse diameters.
- Stacks equal to or less than 0.6 m (24 in.): Follow the procedure above noting only that the "adjusted" points should be relocated at 1.27 cm (0.5 in.) from the wall instead of 2.54 cm (1 in.).

Rectangular stacks. Divide the cross section into as many equal rectangular areas as traverse points, such that the ratio of the length to the width of the elemental areas is between one and two. Locate the traverse points at the centroid of each equal area according to the example in Figure 5-6.

d) Verification of Non-Cyclonic or Non-Swirling Flow

Generally, cyclonic or swirling flow can be expected after such devices as cyclones and inertial demisters that follow venturi scrubbers or in stacks that have tangential inlets or two inlets that are opposite each other. At times, cyclonic flow can be detected by visual observations of the effluent plume. However, a Type S pitot tube as described in Method 2 can be used as a tool to verify the presence of cyclonic or swirling flow by doing the following:

Level and zero the manometer. Position the Type S pitot tube at each of the traverse points such that the face openings are perpendicular to the stack cross-sectional plane. A null (zero) reading at "0^0 reference" denotes the absence of cyclonic flow. If the reading is not zero, then rotate the pitot tube about $\pm 10^0$. A null reading within the limits of $\pm 10^0$ rotation from 0^0 reference indicates an acceptable flow condition.

Conduct a velocity traverse according to Method 2. If there are negative velocity pressure readings, ensure that the pitot lines are not reversed.

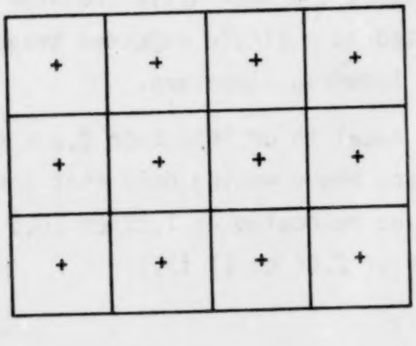


Figure 5-6. Example Showing Rectangular Stack Cross Section Divided into 12 Equal Areas, with Traverse Points at Centroid of Each Area

5.2.9.4 Method 2 - Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube)

1) Principle and applicability

Stack gas velocity is determined from the gas density and from measurement of the velocity head using a Type S (Stausscheibe or reverse type) pitot tube. This method is applicable for measurement of the average velocity of a gas stream and for quantifying gas flow. This procedure is not applicable for direct measurement in cyclonic or swirling gas streams. (Method 1, section 2, d, shows how to determine unacceptable flow conditions.)

2) Apparatus

a) Pitot Tube

Type S (Figure 5-7), or equivalent, calibrated according to the procedure in section 4.

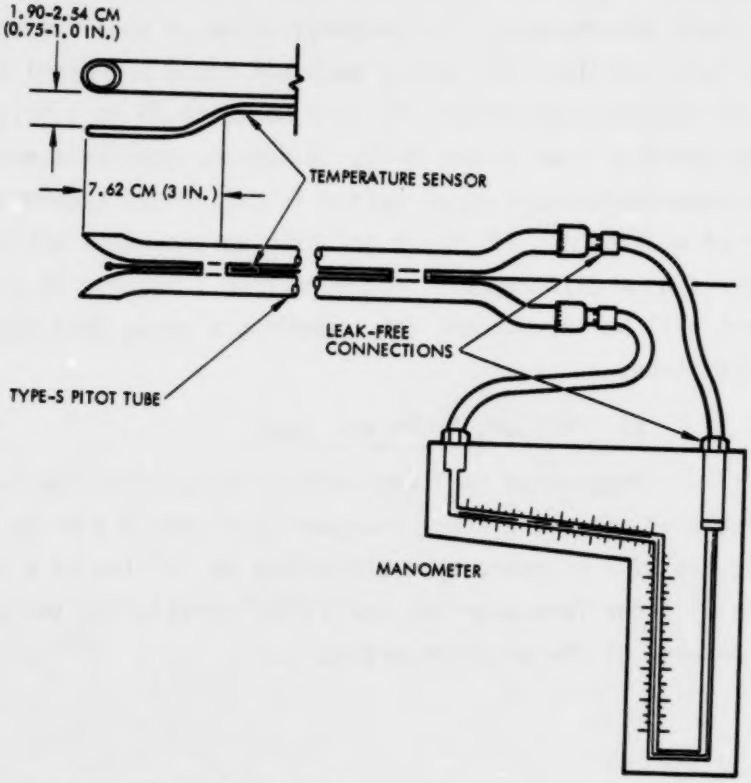

1.90-2.54 CM
(0.75-1.0 IN.)
7.62 CM (3 IN.)
TEMPERATURE SENSOR
LEAK-FREE CONNECTIONS
TYPE-S PITOT TUBE
MANOMETER

Figure 5-7. Pitot Tube-Manometer Assembly

b) Differential Pressure Gauge

Inclined manometer, or equivalent device, capable of measuring velocity head to within 10 percent of the minimum measured value or ±0.013 mm (0.005 in.), whichever is greater. Below a differential pressure of 1.3 mm (0.5 in.) water gauge, micromanometers with sensitivities of 0.013 mm (0.0005 in.) should be used. However, micromanometers may not easily be adaptable to the existing field conditions and are not easy to use with pulsating flow.

The calibration of magnehelics, if used, must be checked after each test series against an oil manometer to agree within 5 percent as specified in the Federal Register.

c) Temperature Gauge

Thermocouple, liquid-filled bulb thermometer, bimetallic thermometer, mercury-in-glass thermometer, or other gauges that are capable of measuring temperature to within 1.5 percent of the minimum absolute stack temperature. The temperature gauge shall be attached to the pitot tube such that the sensor does not touch any metal and its position is adjacent and about 1.90 to 2.54 cm (0.75 to 1 in.) from the pitot tube openings (see Figure 5-7). Alternate positions may be used if the pitot tube-temperature gauge system is calibrated according to the procedure of section 4. If it can be shown to the satisfaction of the Test Leader that a difference of not more than 1 percent in the velocity measurement will be introduced, the temperature gauge need not be attached to the pitot tube.

d) Pressure Probe and Gauge

Piezometer tube and mercury or water-filled U-tube manometer capable of measuring stack pressure to within 2.5 mm Hg (0.1 in. Hg). The static tap of a standard type pitot tube or one leg of a Type S pitot tube with the face openings positioned parallel to the gas flow may also be used as the pressure probe.

e) Barometer

Mercury, aneroid or other barometers capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby weather bureau station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment of elevation differences between the weather station and the sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft.) elevation increase or vice versa for elevation decrease.

f) Gas Analyzer

Shimadzu GC-3BT chromatograph with dual thermal conductivity detectors as described in section 6.2.5 under field analysis.

g) Calibration Pitot Tube, Standard Type

The standard type pitot tube shall have a known coefficient obtained from the National Bureau of Standards, Route 70 S, Quince Orchard Road, Gaithersburg, Maryland. An alternative is to use a Prandtl type pitot tube designed according to the criteria given below and illustrated in Figure 5-8; which ensure that its coefficient will be 0.99 ±0.01.

- Hemispherical or ellipsoidal tip (inlet end of the impact tube).

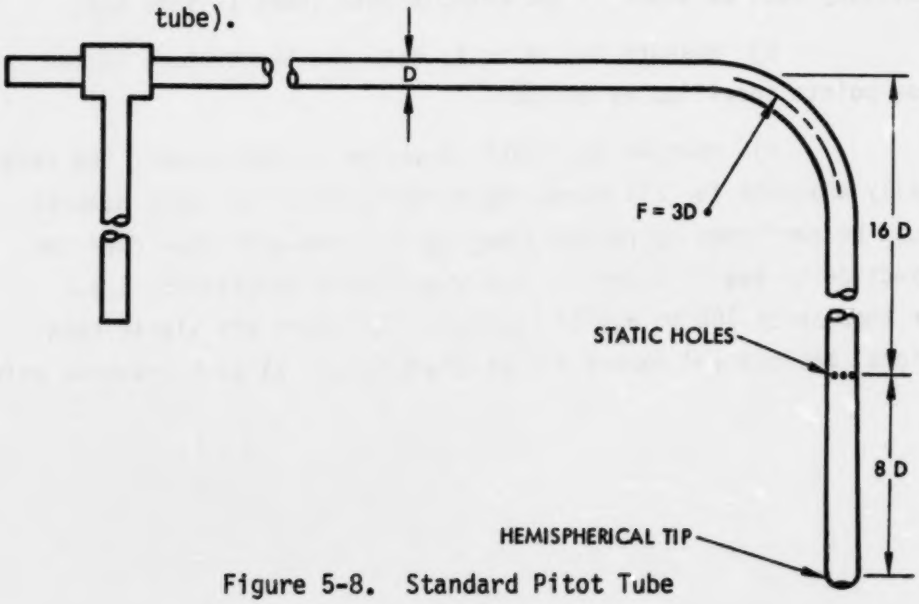


Figure 5-8. Standard Pitot Tube

- Eight diameters of straight run (based on the diameter of the external tube) between the tip and the static pressure holes.
- Sixteen diameters between the static pressure holes and the centerline of the external tube, following the 90° bend.
- Eight static pressure holes of equal size (approximately 0.71 mm or 1/32 in. diameter), equally spaced in a piezometer ring configuration.
- Ninety-degree bend of relatively large radius (approximately three diameters).

h) Calibration Differential Pressure Gauge

For calibration purposes, inclined manometer, or equivalent device capable of measuring velocity head to within 0.13 mm H_2O (0.005 in. H_2O).

3) Procedure

a) Set up the apparatus as shown in Figure 5-7. Make sure all connections are tight and leak free. Level and zero the manometer. Because the manometer level and zero may drift due to vibration and temperature changes, make periodic checks during the sample run. Record all necessary data as shown in the example data sheet (Figure 5-9).

b) Measure the velocity head and temperature at the traverse points specified by Method 1.

c) Measure the static pressure in the stack. One reading is usually adequate for all measuring points during the test; however, this must be confirmed by randomly moving the pressure probe over the cross section to see if there are any significant variations, i.e., greater than about 100 mm H_2O (4 in. H_2O). If there are significant variations, measure and record the static pressure at each traverse point.

PLANT ____________________

DATE ____________ RUN NO. ____________

STACK DIAMETER OR DIMENSIONS, m(in.) ____________

BAROMETRIC PRESSURE, mm Hg (in. Hg) ____________

CROSS SECTIONAL AREA, $m^2(ft^2)$ ____________

OPERATORS ____________

PITOT TUBE I.D. NO. ____________

AVG. COEFFICIENT, C_p = ____________

LAST DATE CALIBRATED ____________

SCHEMATIC OF STACK CROSS SECTION

Traverse Pt. No.	Vel. Hd., Δp mm (in.) H_2O	Stack Temperature		P_g* mm Hg (in.Hg)	$\sqrt{\Delta p}$
		t_s, °C (°F)	T_s, °K (°R)		
		Average			

*If preliminary investigation shows that P_g varies no more than 100 mm H_2O (4 in. H_2O), record one reading.

Figure 5-9. Velocity Traverse Data

d) Determine the atmospheric pressure.

e) Determine the dry stack gas molecular weight. This may be done either by plant run data or by GC data as derived in section 6.2.

f) Determine the moisture content by either plant run data or by stoichiometric calculation.

g) Determine the cross sectional area of the stack or duct at the sampling location. Whenever possible, it is better to physically measure the stack dimensions rather than using blueprints.

4) Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

A = Cross sectional area of stack, m^2 (ft^2)

B_{wa} = Water vapor in the gas stream, proportion by volume

C_p = Pitot tube coefficient, dimensionless

K_p = Pitot tube constant,

$$34.97 \frac{m}{sec}\left[\frac{(g/g\text{-mole})(mm\ Hg)}{(^{o}K)(mm\ H_2O)}\right]^{1/2}$$

for the metric system and

$$85.48 \frac{ft}{sec}\left[\frac{(lb/lb\text{-mole})(in.\ Hg)}{(^{o}R)(in.\ H_2O)}\right]^{1/2}$$

for the English system

M_d = Molecular weight of stack gas, dry basis, g/g-mole (lb/lb-mole)

M_s = Molecular weight of stack gas, wet basis, g/g-mole (lb/lb-mole)

$= M_d (1 - B_{wa}) + 18\ B_{wa}$

P_{bar} = Atmospheric pressure, mm Hg (in. Hg)

P_g = Stack static pressure, mm Hg (in. Hg)

P_s = Absolute stack gas pressure, mm Hg (in. Hg)

= $P_{bar} + P_g$

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg)

Q_{sd} = Dry, volumetric stack gas flow rate corrected to standard conditions, dscm/hr (dscf/hr)

t_s = Stack temperature, ^oC (^oF)

T_s = Absolute stack temperature, ^oK (^oR)

= $273 + t_s$ for metric

= $460 + t_s$ for English

T_{std} = Standard absolute temperature, 293^oK (528^oR)

v_s = Average stack gas velocity, m/sec (ft/sec)

Δp = Velocity head of stack gas, mm H_2O (in. H_2O)

3600 = Conversion factor, sec/hr

18 = Molecular weight of water, g/g-mole (lb/lb-mole)

Average stack gas velocity.

$$v_s = K_p C_p (\sqrt{\Delta p})_{avg} \left(\frac{(T_s)_{avg}}{P_s M_s} \right)^{1/2}$$

Average stack gas dry volumetric flow rate.

$$Q_{sd} = 3600 \ (1 - B_{wa}) \ V_g A \left[\frac{T_{std}}{T_{s(avg)}} \right] \left[\frac{P_s}{P_{std}} \right]$$

The quantities of sample needed in order to perform the required analyses are presented earlier. Naturally, the knowledge of whether or not these quantities have been acquired during the run cannot be obtained until subsequent gravimetric analyses have been performed. For this reason the PMB has developed a series of sampling guidelines criteria for acquiring the required quantity of sample during each run. These criteria are:

- At least one combustion process cycle and 30 standard m^3 (1060 scf) of the process effluent are to be sampled during each run.
- In the event that the combustion process is not cyclic in nature, the 30 standard m^3 figure must still be satisfied over a period of time conducive to obtaining a sample representative of process conditions. A sampling duration of five hours has satisfied this requirement in the past.

To fulfill the above conditions it may be necessary on several occasions (due to high grain loading conditions) to interrupt the progress of the run to change the filter or nozzle due to clogging problems. Indicate start and stop times on run sheets and extend run time to maintain a total of 30 m^3 of gas collection. This is an acceptable procedure, however, care must be taken to avoid contamination in the process of transfer. A detailed log should be kept to record any relevant conditions pertaining to the change.

5.2.10 Filter Changing and Transfer

To fulfill the sampling requirements it may be necessary on several occasions (depending on grain loading conditions) to interrupt the sampling run to change the filter as a result of clogging problems. This will be required whenever it is no longer possible to maintain flow by throttling the pump. Filter transfer tends to be a time-consuming process which may require as much as 1.5 to 2 hours depending on sampler location as well as possible difficulties which may be encountered in removing the housing. Once removed, the housing must be carried intact to the clean area of the van for transfer. Care must be taken to avoid contamination in the process of the transfer. The filter is to be transferred to a clean, tared, 150 x 15 mm plastic petri dish. In each case the clean filter and petri dish are tared together so that a final weight may be obtained in the laboratory. The non-sampling time lapse is to be added to the overall sampling duration and is to be duly recorded on the run sheet.

5.2.11 Sample Handling and Transfer

The procedures used in transfering acquired sample from various portions of the SASS train are extremely involved. To expedite the explanation of the procedures involved in sample transfer and handling, the subject is discussed in terms of a modular approach. For this reason, the SASS train is considered in terms of the following sections:

1) Nozzle and probe
2) Cyclone system interconnect tubing
3) Cyclones and filter
4) XAD-2 module
5) Impingers

At the conclusion of the sampling run, the train is disassembled and transported to the mobile lab unit or prepared work area as follows:

1) Open the cyclone oven to expedite cooling, disconnect the probe and cap off both ends.

2) Disconnect the line joining the cyclone oven to the XAD-2 module at the exit side of the filter and cap off:

   a) The entrance to the 10μ cyclone,

   b) The filter holder exit, and

   c) The entrance to the join line which was disconnected from the filter holder exit point.

3) Disconnect the line joining the XAD-2 module to the impinger system at the point where it exits and XAD-2 module. Cap off the exit of the XAD-2 module and the entrance line to the impinger system.

4) Disconnect the line exiting the silica gel impinger at the point where it leaves the impinger and cap off the impinger box to facilitate carrying.

The solvent system to be used for line rinse and final clean-out of adhered sample consists of a 51%/49% mixture of methylene chloride and acetone.

Since step-by-step procedural instruction in narrative form would be voluminous, time-consuming to follow, and might be confusing to the reader, each step is presented in the following series of flow diagrams (Figures 5-10 to 5-12). These diagrams will be placed in an easily visible location near the cleaning area in the van as an aid to the sample transfer activity.

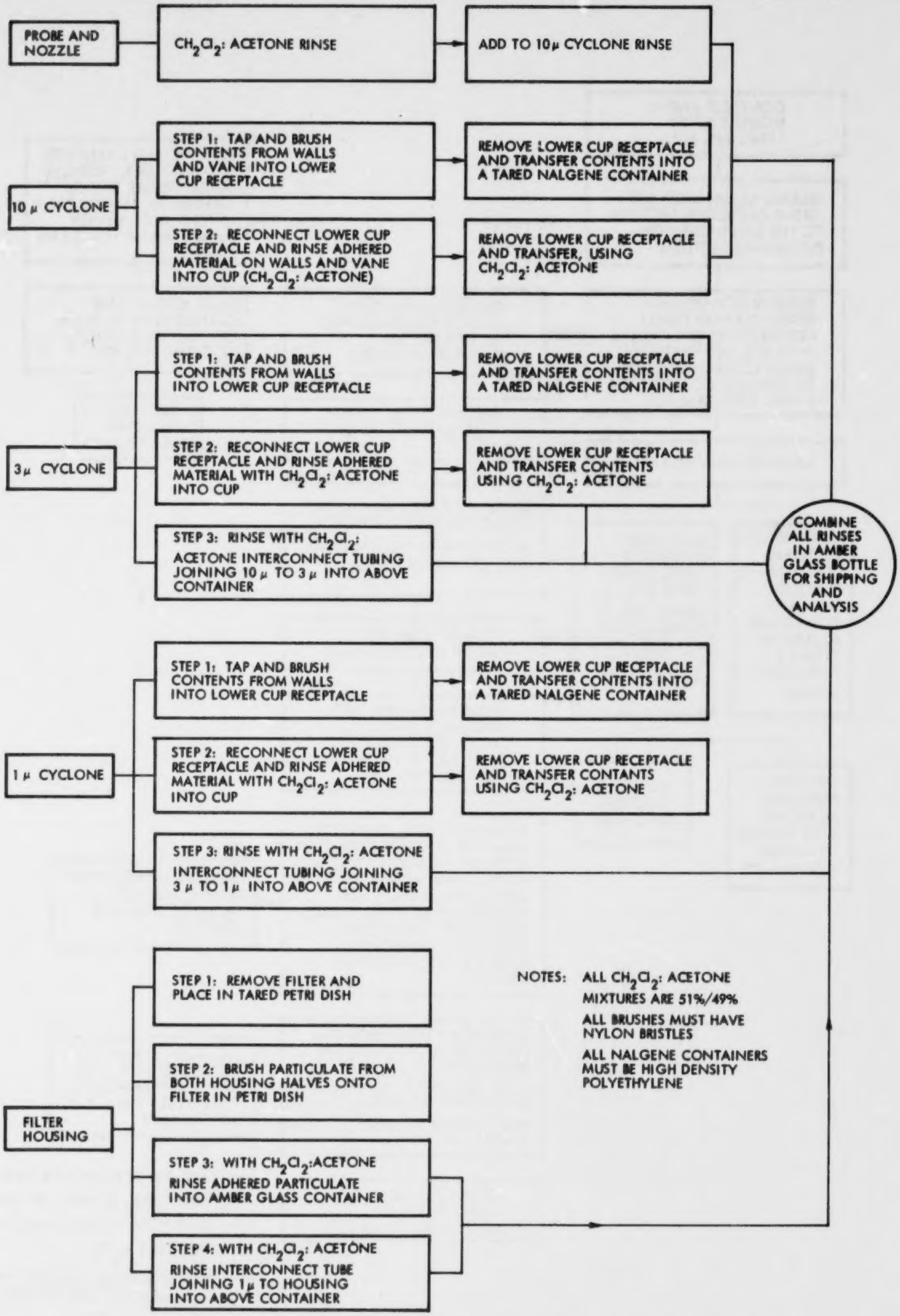
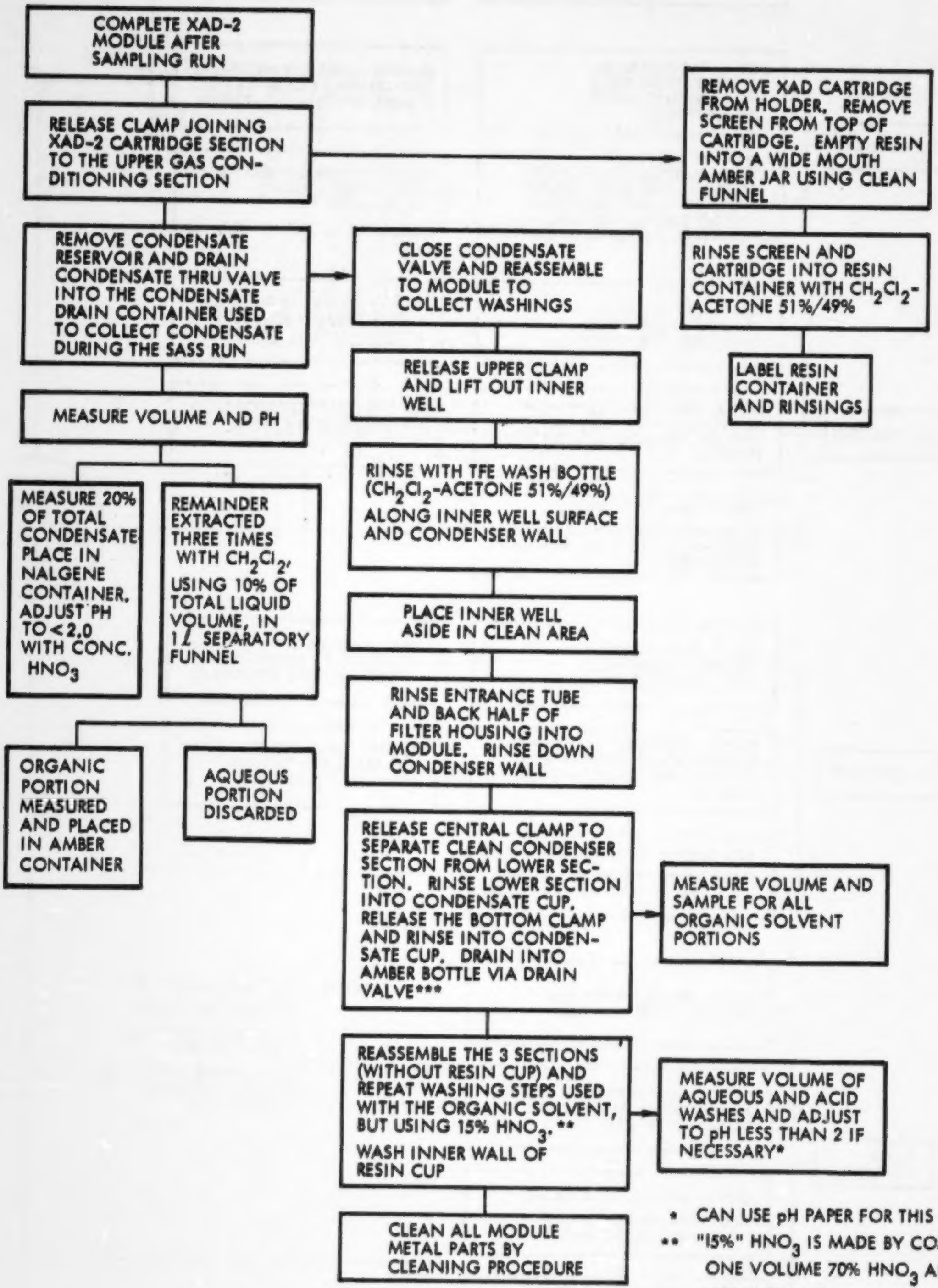

PROBE AND NOZZLE
CH_2Cl_2: ACETONE RINSE
ADD TO 10μ CYCLONE RINSE
10 μ CYCLONE
STEP 1: TAP AND BRUSH CONTENTS FROM WALLS AND VANE INTO LOWER CUP RECEPTACLE
REMOVE LOWER CUP RECEPTACLE AND TRANSFER CONTENTS INTO A TARED NALGENE CONTAINER
STEP 2: RECONNECT LOWER CUP RECEPTACLE AND RINSE ADHERED MATERIAL ON WALLS AND VANE INTO CUP (CH_2Cl_2: ACETONE)
REMOVE LOWER CUP RECEPTACLE AND TRANSFER, USING CH_2Cl_2: ACETONE
3μ CYCLONE
STEP 1: TAP AND BRUSH CONTENTS FROM WALLS INTO LOWER CUP RECEPTACLE
REMOVE LOWER CUP RECEPTACLE AND TRANSFER CONTENTS INTO A TARED NALGENE CONTAINER
STEP 2: RECONNECT LOWER CUP RECEPTACLE AND RINSE ADHERED MATERIAL WITH CH_2Cl_2: ACETONE INTO CUP
REMOVE LOWER CUP RECEPTACLE AND TRANSFER CONTENTS USING CH_2Cl_2: ACETONE
STEP 3: RINSE WITH CH_2Cl_2: ACETONE INTERCONNECT TUBING JOINING 10 μ TO 3 μ INTO ABOVE CONTAINER
COMBINE ALL RINSES IN AMBER GLASS BOTTLE FOR SHIPPING AND ANALYSIS
1 μ CYCLONE
STEP 1: TAP AND BRUSH CONTENTS FROM WALLS INTO LOWER CUP RECEPTACLE
REMOVE LOWER CUP RECEPTACLE AND TRANSFER CONTENTS INTO A TARED NALGENE CONTAINER
STEP 2: RECONNECT LOWER CUP RECEPTACLE AND RINSE ADHERED MATERIAL WITH CH_2Cl_2: ACETONE INTO CUP
REMOVE LOWER CUP RECEPTACLE AND TRANSFER CONTANTS USING CH_2Cl_2: ACETONE
STEP 3: RINSE WITH CH_2Cl_2: ACETONE INTERCONNECT TUBING JOINING 3 μ TO 1 μ INTO ABOVE CONTAINER
FILTER HOUSING
STEP 1: REMOVE FILTER AND PLACE IN TARED PETRI DISH
STEP 2: BRUSH PARTICULATE FROM BOTH HOUSING HALVES ONTO FILTER IN PETRI DISH
STEP 3: WITH CH_2Cl_2:ACETONE RINSE ADHERED PARTICULATE INTO AMBER GLASS CONTAINER
STEP 4: WITH CH_2Cl_2: ACETONE RINSE INTERCONNECT TUBE JOINING 1μ TO HOUSING INTO ABOVE CONTAINER
NOTES: ALL CH_2Cl_2: ACETONE MIXTURES ARE 51%/49%
ALL BRUSHES MUST HAVE NYLON BRISTLES
ALL NALGENE CONTAINERS MUST BE HIGH DENSITY POLYETHYLENE

Figure 5-10. Sample Handling and Transfer - Nozzle, Probe, Cyclones and Filter


COMPLETE XAD-2 MODULE AFTER SAMPLING RUN
RELEASE CLAMP JOINING XAD-2 CARTRIDGE SECTION TO THE UPPER GAS CONDITIONING SECTION
REMOVE XAD CARTRIDGE FROM HOLDER. REMOVE SCREEN FROM TOP OF CARTRIDGE. EMPTY RESIN INTO A WIDE MOUTH AMBER JAR USING CLEAN FUNNEL
RINSE SCREEN AND CARTRIDGE INTO RESIN CONTAINER WITH CH_2Cl_2-ACETONE 51%/49%
LABEL RESIN CONTAINER AND RINSINGS
REMOVE CONDENSATE RESERVOIR AND DRAIN CONDENSATE THRU VALVE INTO THE CONDENSATE DRAIN CONTAINER USED TO COLLECT CONDENSATE DURING THE SASS RUN
CLOSE CONDENSATE VALVE AND REASSEMBLE TO MODULE TO COLLECT WASHINGS
MEASURE VOLUME AND PH
RELEASE UPPER CLAMP AND LIFT OUT INNER WELL
MEASURE 20% OF TOTAL CONDENSATE PLACE IN NALGENE CONTAINER. ADJUST PH TO <2.0 WITH CONC. HNO_3
REMAINDER EXTRACTED THREE TIMES WITH CH_2Cl_2, USING 10% OF TOTAL LIQUID VOLUME, IN 1 ℓ SEPARATORY FUNNEL
RINSE WITH TFE WASH BOTTLE (CH_2Cl_2-ACETONE 51%/49%) ALONG INNER WELL SURFACE AND CONDENSER WALL
PLACE INNER WELL ASIDE IN CLEAN AREA
ORGANIC PORTION MEASURED AND PLACED IN AMBER CONTAINER
AQUEOUS PORTION DISCARDED
RINSE ENTRANCE TUBE AND BACK HALF OF FILTER HOUSING INTO MODULE. RINSE DOWN CONDENSER WALL
RELEASE CENTRAL CLAMP TO SEPARATE CLEAN CONDENSER SECTION FROM LOWER SECTION. RINSE LOWER SECTION INTO CONDENSATE CUP. RELEASE THE BOTTOM CLAMP AND RINSE INTO CONDENSATE CUP. DRAIN INTO AMBER BOTTLE VIA DRAIN VALVE***
MEASURE VOLUME AND SAMPLE FOR ALL ORGANIC SOLVENT PORTIONS
REASSEMBLE THE 3 SECTIONS (WITHOUT RESIN CUP) AND REPEAT WASHING STEPS USED WITH THE ORGANIC SOLVENT, BUT USING 15% HNO_3.** WASH INNER WALL OF RESIN CUP
MEASURE VOLUME OF AQUEOUS AND ACID WASHES AND ADJUST TO pH LESS THAN 2 IF NECESSARY*
CLEAN ALL MODULE METAL PARTS BY CLEANING PROCEDURE

* CAN USE pH PAPER FOR THIS STEP

** "15%" HNO_3 IS MADE BY COMBINING ONE VOLUME 70% HNO_3 AND FOUR VOLUMES H_2O.

*** THIS PROCEDURE ENSURES MATING LIPS OF EQUIPMENT ARE PROPERLY CLEANED.

Figure 5-11. Sample Handling and Transfer - XAD-2 Module

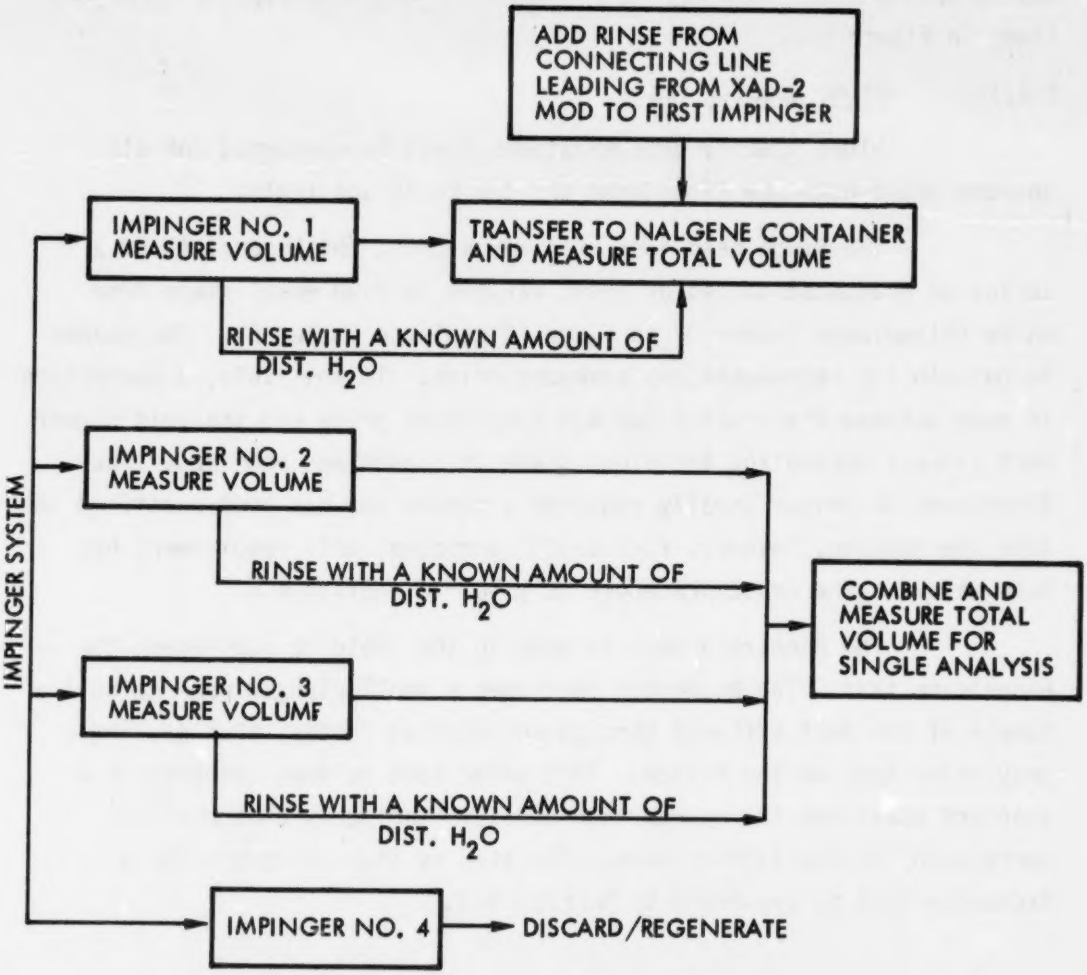

ADD RINSE FROM CONNECTING LINE LEADING FROM XAD-2 MOD TO FIRST IMPINGER
IMPINGER SYSTEM
IMPINGER NO. 1 MEASURE VOLUME
TRANSFER TO NALGENE CONTAINER AND MEASURE TOTAL VOLUME
RINSE WITH A KNOWN AMOUNT OF DIST. H2O
IMPINGER NO. 2 MEASURE VOLUME
RINSE WITH A KNOWN AMOUNT OF DIST. H2O
COMBINE AND MEASURE TOTAL VOLUME FOR SINGLE ANALYSIS
IMPINGER NO. 3 MEASURE VOLUMF
RINSE WITH A KNOWN AMOUNT OF DIST. H2O
IMPINGER NO. 4
DISCARD/REGENERATE

Figure 5-12. Sample Handling and Transfer-Impingers.

Samples will be shipped by the most expeditious manner and will not be delayed unnecessarily.

At the completion of all sample transfer activities, all SASS train components must be completely re-cleaned in preparation for the next sampling run. This may be accomplished by following the steps outlined in Figure 5-2.

5.2.12 Plume Opacity Tests

Plume opacity determinations shall be conducted for all sources using both the Ringelmann and the Bacharach tests.

The Ringelmann test utilizes a chart which consists of a series of graduated shades of grey, varying in five equal steps from white (Ringelmann Number 0) to black (Ringelmann Number 5). The shades in between are represented by standard grids. In the field, a comparison is made between the stack plume and Ringelmann grids and the grid number most closely resembling the plume shade is chosen and recorded. The Ringelmann technique usually requires a person who has been certified to take the reading; however, for Level 1 purposes, this requirement has been waived. The exact procedure is given in section 6.6.

The Bacharach test is used in the field to supplement the Ringelmann test. The Bacharach test uses a small plunger pump to pull a sample of the duct effluent through an inserted filter, thus causing a gray color spot on the filter. This color spot is then compared to a standard scale and the appropriate density reading is chosen which corresponds to the filter shade. The step by step procedure for a Bacharach test is presented in Section 6.7.

5.3 GAS SAMPLING

Gas samples are taken using an integrated gas sampling train. The gas sample is drawn through a stainless steel probe and an ice bath condenser. Two methods are used. See Figure 5-13 for Method I and Figures 5-14 and 5-15 for Method II.

5.3.1 Method I

a. Apparatus:

- Probe - Stainless steel probe containing a glass wool filter to remove particulate matter.
- Condenser - Water cooled condenser to remove excess moisture.
- Valve - Needle valve to adjust sample gas flow.
- Pump - Leak-free, diaphragm-type or equivalent, to transport sample gas to Tedlar bag.
- Bag - Tedlar sample bag.
- Flow meter - Capable of measuring 0.5 ℓ/min.

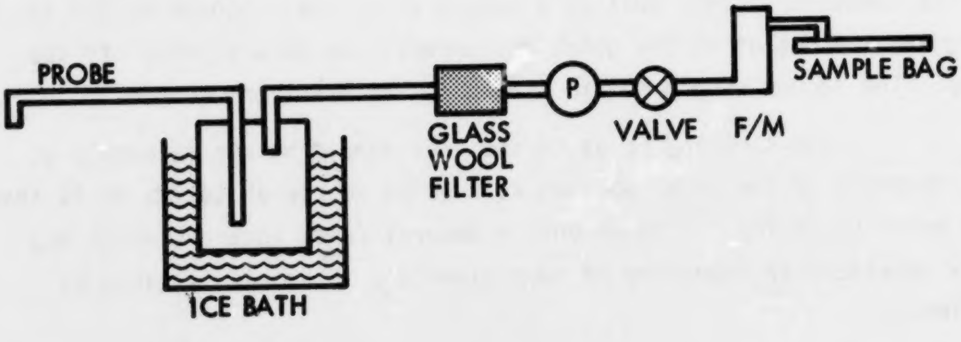


Figure 5-13. Integrated Gas-Sampling Train - Method I

5.3.2 Method II

a. Apparatus:

- Probe - Same as Method I w/filter.
- Condenser - Same as Method I.
- Valve - Same as Method I.
- Pump - High volume vacuum pump.
- Bag - Same as Method I.
- Flow meter - Same as Method I.
- Steel drum - Drum equipped with Swagelok quick disconnect female connectors.

5.3.3 Reagents

None

5.3.4 Sampling Procedure

Prior to field use, all Polymer sandwiched aluminum bags are to be leak checked. The bags are leak checked by inflating them to a pressure of 5 to 10 cm H_2O (2-4 in. H_2O) as determined by an in-line manometer. Any displacement in the manometer after a 10-minute time interval indicates a leak. In the field prior to the sampling operation, the train is also leak checked. This is done by placing a vacuum gauge at the condenser inlet, pulling a vacuum of at least 250 mm Hg (10 in. Hg), plugging the outlet at the quick disconnect, and then turning off the pump. The vacuum should remain stable for at least one minute.

The sampling point in the duct should be approximately at the centroid of the cross section at a point no closer to the walls than one meter (3.28 ft). This is only a general rule, however, which may vary considerably depending on duct diameter. A sample is taken as follows:

- Place the probe in the stack at the sampling point and then purge the sampling line up to the bag.
- Connect the bag and make sure that all connections are tight and leak free.
- Flush sample bag three times with sample.

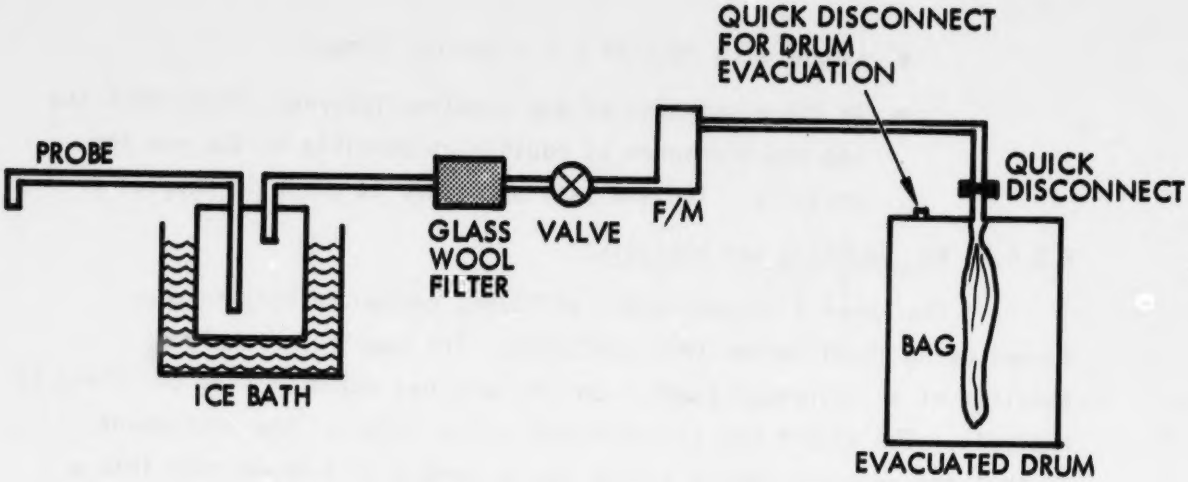

QUICK DISCONNECT
FOR DRUM
EVACUATION
PROBE
QUICK
DISCONNECT
GLASS
WOOL
FILTER
VALVE
F/M
BAG
ICE BATH
EVACUATED DRUM

Figure 5-14. Integrated Gas Sampling Train - Method II.

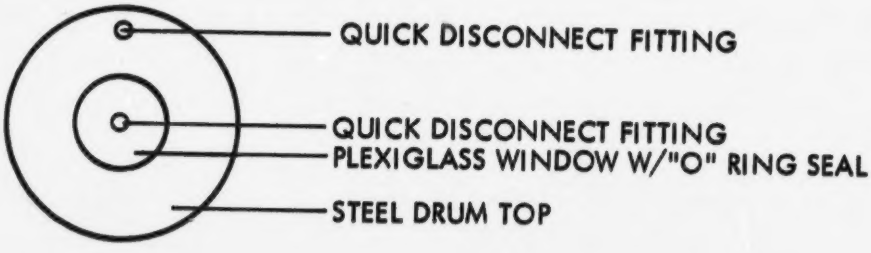

QUICK DISCONNECT FITTING
QUICK DISCONNECT FITTING
PLEXIGLASS WINDOW W/"O" RING SEAL
STEEL DRUM TOP

Figure 5-15. Method II Steel Drum Top View

- Sample at a rate of 0.5 liter per minute.
- At the conclusion of the sampling interval, disconnect the bag and transport as rapidly as possible to the van for analysis. The analysis procedure is given in Chapter 6.

5.3.4.1 NO_x Sampling and Analysis*

The Level 1 determination of NO/NO_2 concentrations is performed using chemiluminescence analyzers. The sample for analysis consists of an increment taken from the same bag which is used for field GC analysis. The sample bag is connected to the inlet of the instrument so that the required sample volume can be pumped at a known rate into a properly calibrated analyzer. The instrument response is then recorded. Depending upon the instrument, the readout can be directly in concentration units. The primary consideration for chemiluminescence instruments involves the calibration procedure which must be carried out on a daily basis while in the field. This procedure is to be done in accordance with the manufacturer's specifications. The manufacturer's manual should be consulted to avoid interference from water and ammonia.

5.3.4.2 NO_x Sampling and Analysis

EPA Method 7 will be employed after 27 July 1978 for NO_x sampling and analysis. The full Federal Register text for NO_x is given in Appendix C.

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*This procedure was utilized prior to July 27, 1978 and discontinued because of NO_x loss in gas bag gives low and unreliable results.

5.4 LIQUID AND SLURRY SAMPLING

5.4.1 Scope and Application

The methods presented in this section are applicable to obtaining representative samples of the following:

- Cooling tower water – sample to be taken from the input and output stream to the tower.
- Cooling water (no cooling towers present) – sample to be taken from input and output streams.
- Boiler blowdown streams – sample to be taken after condensation.
- Slurries – from wet ash sluicing or bottom ash handling; sample from sluice or scrubber outlet.
- Evaporation pond – samples taken away from the shore boundary.
- Settling pond – overflows, if present.

The need, application, and analysis for each type of sample is given in Chapter 3, Section 3.8.

5.4.2 Summary of Methods and General Considerations

Any of the above four groups may be sampled by one or more of the following three methods depending on sample consistency: 1) tap sampling, 2) heat exchange sampling, and 3) dipper sampling. Detailed procedures for each of these three methods are presented in this section.

For the purposes of this assessment effort, liquids will be distinguished from slurries by a solids content value of <5%. This value is intended only to be used as a decision guideline for sampling procedure selection and consequently must be chosen subjectively. The same is true for the temperature value of 50°C which is chosen primarily for safety reasons. A decision matrix relating stream condition to sampling procedures for liquids and slurries is presented in Figure 5-16.

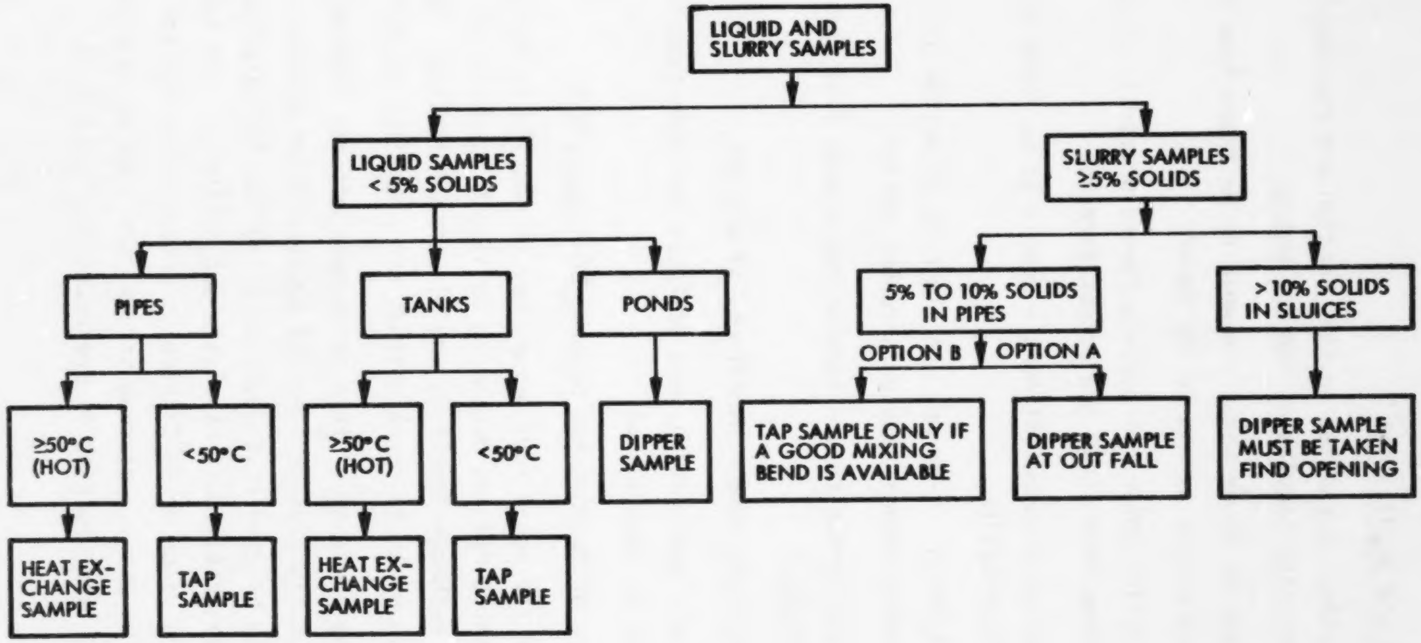
LIQUID AND SLURRY SAMPLES
LIQUID SAMPLES < 5% SOLIDS
SLURRY SAMPLES ≥5% SOLIDS
PIPES
TANKS
PONDS
5% TO 10% SOLIDS IN PIPES
>10% SOLIDS IN SLUICES
OPTION B
OPTION A
≥50°C (HOT)
<50°C
≥50°C (HOT)
<50°C
DIPPER SAMPLE
TAP SAMPLE ONLY IF A GOOD MIXING BEND IS AVAILABLE
DIPPER SAMPLE AT OUT FALL
DIPPER SAMPLE MUST BE TAKEN FIND OPENING
HEAT EX-CHANGE SAMPLE
TAP SAMPLE
HEAT EX-CHANGE SAMPLE
TAP SAMPLE

Figure 5-16. Decision Matrix for Liquid/Slurry Sampling

Prior to sampling any liquid stream, plant data concerning the stream must be recorded on a sample log sheet. Many streams exist under pressure or elevated temperature or both; attempts to sample such a stream without prior knowledge of its condition could result in severe injury. The following data points are required from the plant engineer:

- temperature,
- pressure,
- flow rate,
- stream identification (blowdown, cooling tower, etc.), and
- solids content.

The data points required from the sampler are:

- temperature,
- sample volume,
- sampling methods used, and
- observations (sample is cloudy, has odor, etc.).

All samples are to be drawn from a point or area which will provide as nearly a representative sample as possible. A flowing stream containing particulate or insoluble phases will be stratified. The optimum sampling location will, therefore, be located after a bend where turbulent mixing will induce homogeneity. In all cases the main pipe or stream flow must be sampled. Because solids can accumulate in seldom used vent or slipstreams, these lines are not recommended for sample acquisition.

5.4.3 Apparatus

- Tap sampler: A supply of thin wall 6.4 mm Teflon tubing with a complete range of Teflon or stainless steel adapters to fit successively larger tap outlet fittings. Polyethylene bottle, A.H. Thomas Catalog No. 1732-B10, or equivalent.
- Dipper sampler: High-density polyethylene beaker or containers which may be attached to rod extensions to reach ponds and sluices.

- Heat exchange sampler: Same as tap sampler with the addition of a coiled length of Teflon tubing and a container to use as a condenser.
- Sample bottles: A supply of 1-and 2-liter high-density polyethylene bottles for inorganics, and a supply of 2-liter amber glass bottles with Teflon lined lids for organic samples.
- Filter paper: Acid washed, ashless, hard-finish paper sufficiently retentive for fine particulates.
- Separatory funnel: Glass, Teflon stopcock, 1-liter capacity.
- Buchner funnel: 1-liter capacity
- Vacuum flask: 10-liter capacity
- Water aspirator.

5.4.4 Reagents

All reagents are reagent grade.

- Nitric acid
- Sodium hydroxide (0.1 N)
- Distilled water
- Sulfuric acid
- Strong soap solution
- Acetone
- Methylene chloride

5.4.5 Equipment Preparation

Containers intended for sampling industrial water streams must be made of a high-density polyethylene or polypropylene. Plastic bottles for aqueous stream samples should be cleaned by:

a) Detergent wash,
b) Distilled water rinse,
c) Nitric acid, 15% v/v.

d) Distilled water rinse,
e) Acetone rinse, and
f) Blow dry with clean filtered air.

Organic samples, including CH_2Cl_2 extractions, must be placed in amber glass bottles to inhibit sample degradation. These amber glass bottles are cleaned by:

a) Strong soap solution,
b) Liberal tap water rinse,
c) Nitric acid, 15% v/v,
d) Distilled water rinse,
e) Acetone rinse,
f) Methylene chloride rinse, and
g) Drying a clean, hot air stream or placing in an oven at 40°C (140°F).

After the containers have been cleaned, dried and capped, they should be stored in boxes to prevent spurious contamination.

5.4.6 Sampling Procedures

5.4.6.1 Tap Sampling

Tap sampling is generally applicable to contained liquids in motion or static liquids in tanks or drums. Slurries are occasionally sampled using the technique but sample representativeness is unreliable if solids content exceeds 10%.

To acquire a tap sample the valve or stopcock used for sample removal must be fitted with a length of pre-cleaned Teflon tubing long enough to reach the bottom of the sample container. Because of the wide diversity in valve and stopcock nozzle sizes, a full range of male to female and female to male Teflon or stainless steel tube adapters are required. A piece of Teflon tubing sufficient in length to reach to bottom of the sample container is coupled to the appropriate male or female adapter. The adapter is then coupled to the valve or stopcock.

The sample is removed by a stopcock or valve by inserting a clean Teflon line into the sampling bottle so that it touches the bottom. The clean sample bottle should be flushed with sample prior to filling. The sample line flow must be regulated so it does not exceed 500 ml/min after the sample line has been flushed at a rate high enough to remove all sediment and gas pockets. The apparatus used for tap sampling is illustrated in Figure 5-17. If sampling valves or stopcocks are not available, samples may be taken from water-level or gauge-glass drain lines or petcocks.

As indicated previously, caution must be exercised while sampling with this technique. The valve must be cracked slowly to allow for escaping air pockets, and to prevent injury due to toxic or heated streams.

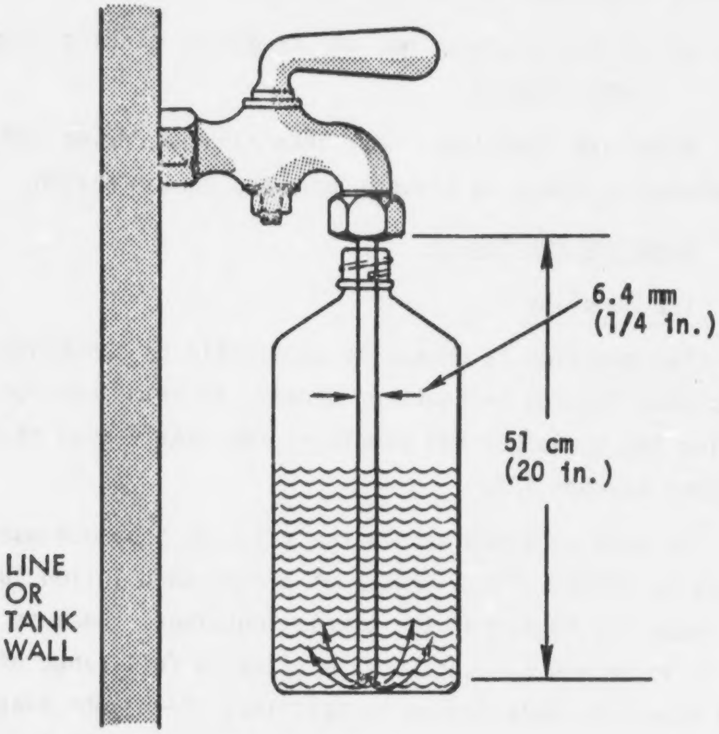

Figure 5-17. Assembly for Tap Sampling

5.4.6.2 Heat Exchange Sampling

No difference exists between this sampling technique and the previous sampling technique except that it applies to streams ≥50°C and therefore requires a condenser coil. The coil is to be constructed from 6.4 mm O.D. Teflon tubing and may be connected directly to the valve or tap or by a coupling. The coil is cooled by immersion into a water circulative or ice condenser. One possible construction of this device is illustrated in Figure 5-18. As in the case of the tap sample, a heat exchange sample is removed from a stopcock or valve by inserting the exit tube of the condenser coil into the sampling bottle so that it touches the bottom. The sample bottle must be thoroughly rinsed with sample prior to filling and sample line flow must be regulated so as not to exceed 500 ml/min after the sample line has been flushed to remove all sediment and gas pockets. This technique is applicable to any liquid stream ≥50°C (122°F).

5.4.6.3 Dipper Sampling

The dipper sampling procedure is applicable to sampling sluices, ponds, or open discharge streams of thick slurry or stratified composition. The dipper is made with a flared bowl and attached handle, long enough to

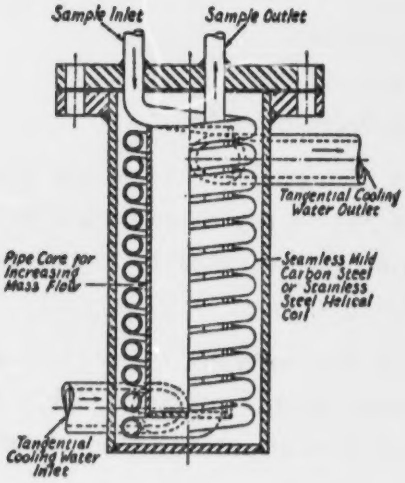
Sample Inlet
Sample Outlet
Tangential Cooling Water Outlet
Pipe Core for Increasing Mass Flow
Seamless Mild Carbon Steel or Stainless Steel Helical Coil
Tangential Cooling Water Inlet

Figure 5-18. Heat Exchange Sampler

reach sluice or discharge areas. The apparatus is constructed of high density polyethylene. The sample is pre-cleaned in accordance with the specifications presented in Section 5.4. 5.

A dipper sample is obtained by inserting the dipper into the free flowing stream so that a portion is collected from the full cross-section of the stream. The optimum position for obtaining this sample will be located directly after a bend where mixing will promote sample homogeneity. If the stream exists in an enclosed or inaccessible sluice, the sample may be taken from the outfall.

Whenever ponds are being sampled, shore and outfall areas are to be avoided since neither of these positions will yield a representative pond sample. The dipper is to be extended as far as possible toward the pond center and the sample is to be removed from this area.

5.4.7 Sample Handling and Shipment

Sample handling where liquids are concerned is an extremely involved operation due to the many possible combinations and analysis considerations applicable to each sample. A liquid or slurry sample may exist in any one of the following six categories:

1) Aqueous,
2) Aqueous/Organic,
3) Organic,
4) Aqueous/Solid,
5) Organic/Solid, or
6) Aqueous/Organic/Solid.

In order to accommodate the various chemical and physical states which may potentially exist in any given sample, a field handling scheme for liquid and slurry samples is presented in Figure 5-19. All samples will be subjected to this handling scheme.

Also, due to the inherent instability of environmentally significant species in acqueous media, stringent field sample preservation steps are required. All sample preservation techniques and handling

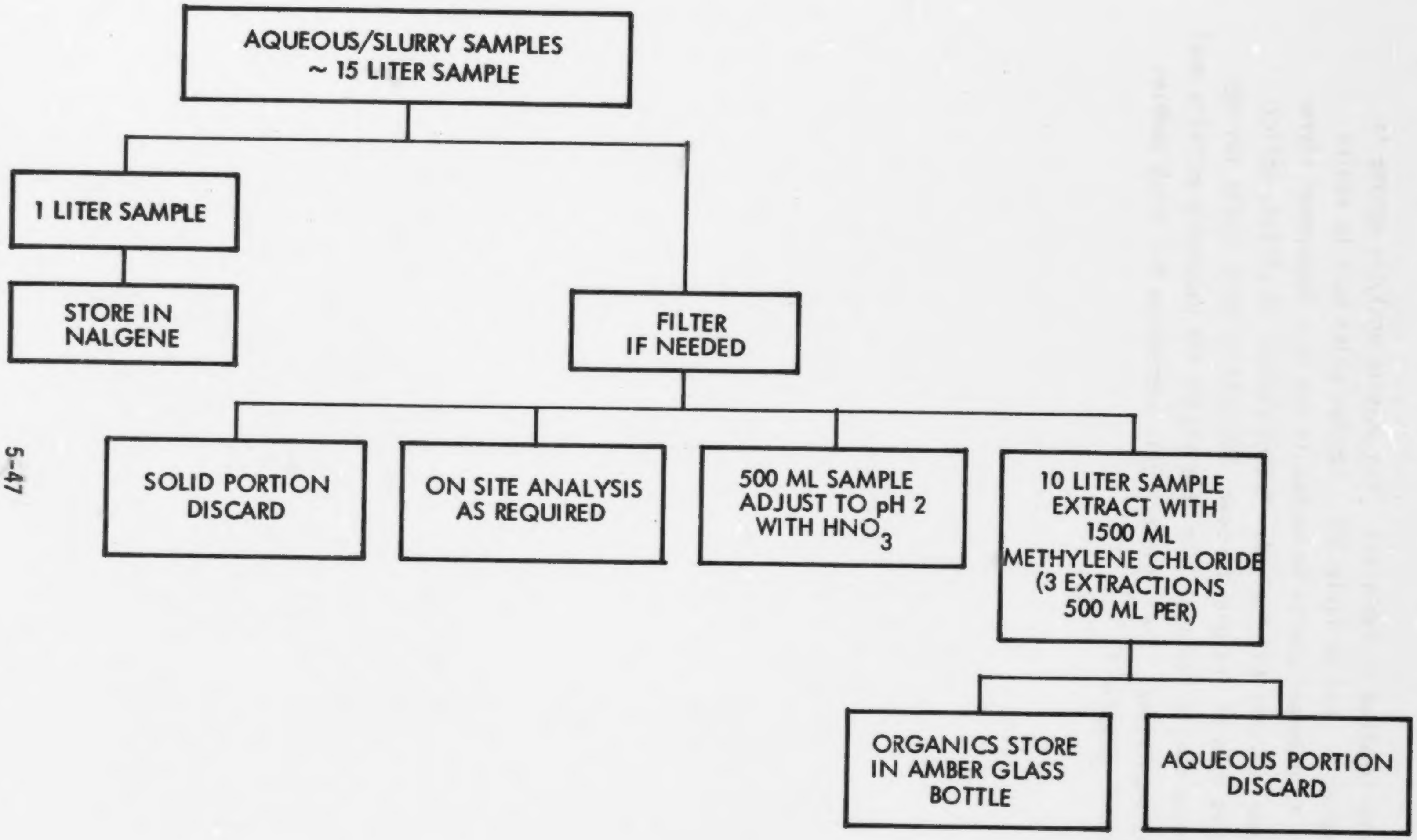
AQUEOUS/SLURRY SAMPLES
~ 15 LITER SAMPLE
1 LITER SAMPLE
STORE IN NALGENE
FILTER IF NEEDED
SOLID PORTION DISCARD
ON SITE ANALYSIS AS REQUIRED
500 ML SAMPLE ADJUST TO pH 2 WITH HNO_3
10 LITER SAMPLE EXTRACT WITH 1500 ML METHYLENE CHLORIDE (3 EXTRACTIONS 500 ML PER)
ORGANICS STORE IN AMBER GLASS BOTTLE
AQUEOUS PORTION DISCARD

Figure 5-19. Field Handling Scheme for Liquid/Slurry Samples

procedures are itemized in Table 5-5. The on-site analysis scheme is shown in Chapter 6 and in Table 3-7. Samples which must be cooled to 4^{0}C prior to shipment are to be packed in ice in a leak-proof styrofoam container and sent air freight. Recent changes in airline policy allow for this type of freight; however, TRW will be held liable for any property damage due to leakage. For this reason the packaging activity must be carefully supervised. The field analysis procedures for these samples are presented in Chapter 6.

Table 5-5. List of Analyses to be Performed on Liquid/Slurry Samples

Analysis	Field Analysis	Lab Analysis	Fraction	Field Preservation Requirements*	Maximum Holding
Acidity	X		Untreated	None Required	24 hours
Alkalinity	X		Untreated	None Required	24 hours
Conductivity	X		Untreated	None Required	24 hours
Suspended Solids	X	X	Untreated	None Required	24 hours
Total Dissolved Solids		X	Untreated	None Required	24 hours
Hardness	X		Untreated	Cool to 4°C	7 days
Water and HCl Leachable Anions		X	Basify	NaOH to pH 12	Depends on Anion
Cations and Elemental Anions		X	Acidify	HNO_3 to pH <2	38 days
pH	X		Untreated	None Required	No holding
Organic Material in Methylene Chloride Extracts		X	Untreated	None Required	7 days
Cyanides	X		Untreated	NaOH to pH of 12	
Ammonia Nitrogen	X		Untreated	H_2SO_4 to pH <2	
Nitrate	X		Untreated	H_2SO_4 to pH <2	24 hours
Phosphate	X		Untreated	None Required	24 hours
Sulfite	X		Untreated	None Required	24 hours
Sulfate	X		Untreated	None Required	7 days

*Preservation and holding requirements applicable only if analysis is not done immediately in field.

5.5 SOLIDS SAMPLING

5.5.1 Scope and Application

This methodology is intended for use in the collection of solid samples associated with combustion sources, such as fly ash, bottom ash, scrubber input materials, and coal feed.

5.5.2 Summary of Methodology

The solid sampling procedure used will be shovel grab samples unless the plant has an automatic sampling system. These techniques are presented in the following sections.

5.5.3 Apparatus

- Square edged shovel, 12 inches wide.
- 1-gallon wide mouth polypropylene (high-density); Thomas Catalog No. 1717 K-22 bottles, or equivalent.

5.5.4 Reagents

None

5.5.5 Procedures

5.5.5.1 Fractional Shovel Grab Samples

The concept of fractional shoveling involves the acquisition of a time integrated grab sample representative of overall process input or output during a given run time period. This procedure uses a standard square edged shovel, 12 inches wide. For streams in motion, either entering or exiting a process operation, a sample is taken from the belt on an hourly basis. A full cross-stream cut should be taken. Each hourly shovel sample is added to a pile to eventually form a run time period composite. At the conclusion of the run this pile will be coned and quartered (as described below in Section 5.5.5.3) to form a final representative sample weighing from 2.3 to 4.5 kilograms (5 to 10 pounds).

It is always preferable to sample a moving stream rather than a stationary storage access. This is particularly true if a large particle or lump size distribution exists in the material. Stored containers or heaped beds of material tend to settle, creating segregation of particles according to size and density, and it is more difficult to account for this bias in the sampling. If it becomes necessary to sample a stationary pile, every attempt should be made to a fully representative sample by taking a number of grab samples from a variety of different areas in the pile.

5.5.5.2 Automatic Samplers

Many plants are equipped with automatic samplers on process input streams. The units are calibrated to remove representative cross sections of a stream while automatically forming a homogeneous composite. Whenever these units are available the sampling team should make use of them in preference to the shovel technique.

5.5.5.3 Coning and Quartering

After a suitable composite has been formed a representative sample for laboratory analysis must be removed. The usual method of accomplishing this task involves the coning and quartering technique.

The coning and quartering procedure involves the following 6 steps:

1) The material is first mixed and formed into a neat cone.

2) The cone is flattened by pressing the top without further mixing.

3) The flat circular pile is then divided into four quarters.

4) The two opposing quarters are discarded.

5) The two remaining quarters are mixed and steps 1-5 are repeated until a 5-10 pound laboratory sample is obtained.

6) The 5-10 pound laboratory sample is to be placed in a 1-gallon wide-mouthed polypropylene bottle, or other suitable containers.

5.6 CONTROLLED CONDENSATION SYSTEM (CCS)

5.6.1 Scope and Application

The Controlled Condensation System (CCS) is designed to measure the vapor phase concentration of SO_3 as H_2SO_4 in controlled or uncontrolled flue gas streams. This method is specifically designed to operate at temperatures up to 250°C (500°F) with 3000 ppm SO_2, 8-16 percent H_2O, and up to 9 g/m^3 (4 gr/cf) of particulate matter.

By using a modified Graham condenser, the gas is cooled to the acid dew point at which the SO_3 (H_2SO_4 vapor) condenses. The temperature of the gas is kept above the water dew point to prevent an interference from SO_2 while a heated quartz filter system removes particulate matter. The condensed acid is then titrated with 0.02 N NaOH using Bromphenol Blue as the indicator.

5.6.2 Reagents

- 30% H_2O_2
- 8% $Na(CO_3)_2$
- Acetone
- Deionized water
- 15% HNO_3

5.6.3 System Design

The SO_3 (H_2SO_4 vapor) Controlled Condensation System (CCS) consists of a heated Vycor probe, a modified Graham condensor (condensation coil), impingers, a pump and a dry test meter (see Figure 5-20)

5.6.4 Preparation

The cleaning procedures for the entire sampling train are systematically listed in Table 5-6.

5.6.5 Sampling

Since a gas, or a small aerosol is being sampled, no traverse will be performed in the stack. It can be shown that the average degree of stratification in the duct is ±15 percent of the mean concentration. Because of the large fluctuation in source emission rates (~50 percent), elimination of the error due to stratification will not significantly

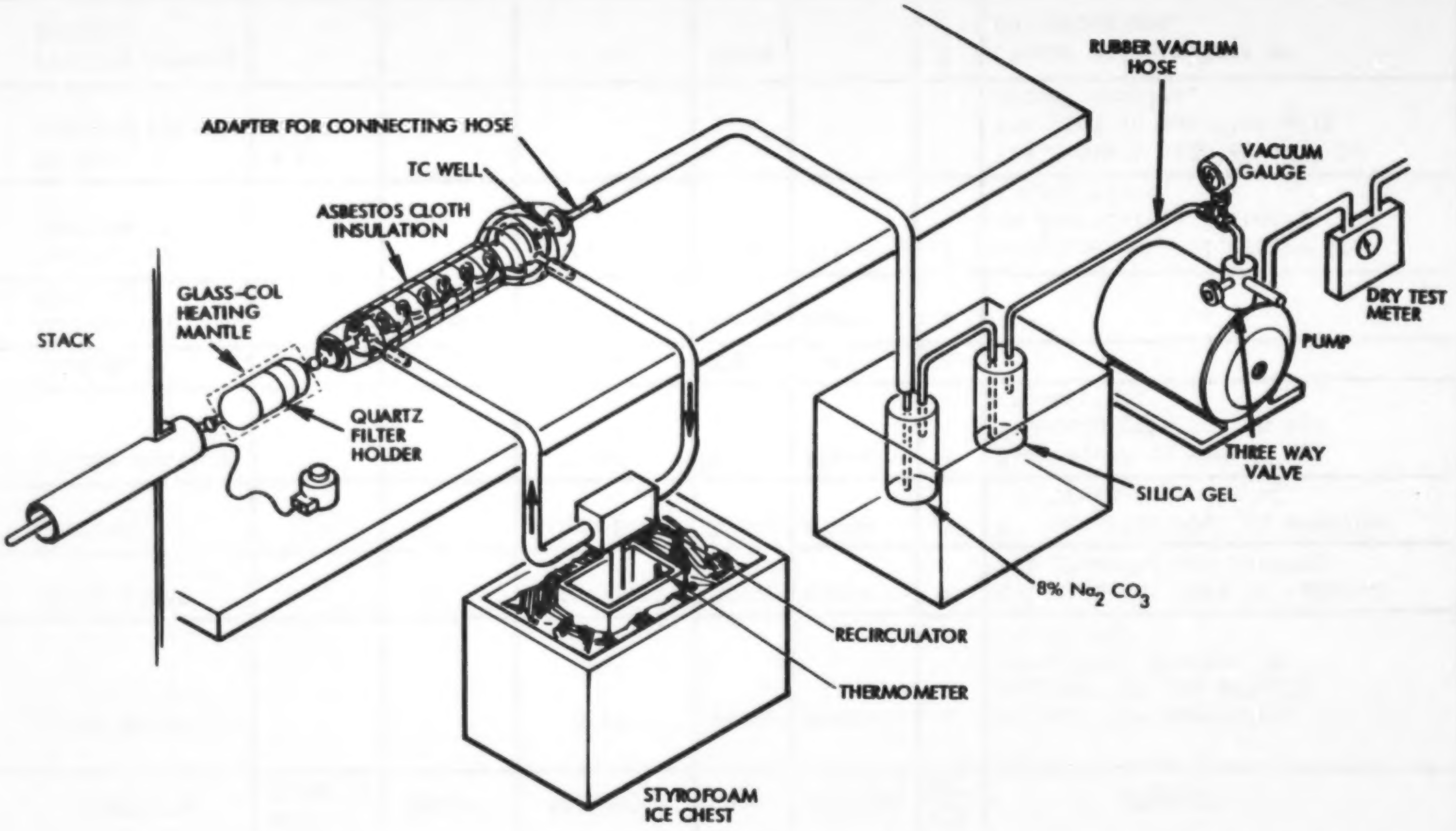
ADAPTER FOR CONNECTING HOSE
TC WELL
ASBESTOS CLOTH INSULATION
GLASS-COL HEATING MANTLE
STACK
QUARTZ FILTER HOLDER
RUBBER VACUUM HOSE
VACUUM GAUGE
DRY TEST METER
PUMP
THREE WAY VALVE
SILICA GEL
8% Na$_2$ CO$_3$
RECIRCULATOR
THERMOMETER
STYROFOAM ICE CHEST

Figure 5-20. Controlled Condensation System Setup

Table 5-6. Cleaning Procedures

COMPONENT	CLEANING PROCEDURES (ORDER APPLIED LEFT TO RIGHT)						REMARKS
	MUFFLE (288°C)	BRUSH	15% HNO_3	H_2O	ACETONE	AIR DRY	
Nylon Brush			3 hr.	Rinse	Rinse	X	Inspect for corrosion, degradation and bristle shredding; discard if any found.
Probe Liner		X	Rinse/Brush	Rinse	Rinse	X	All material must be removed via brushing and rinsing.
Cyclone		X	Rinse/Brush	Rinse	Rinse	X	All material must be removed via brush and rinsing.
Filter Housing			Rinse	Rinse	Rinse	X	Back flush to remove any impacted material in the front/side.
Impingers		Optional	Rinse	Rinse	Rinse	X	
Connecting Glassware		Optional	Rinse	Rinse	Rinse	X	
Controlled Condensation Coil			3 hr./Rinse	Rinse	Rinse	X	HNO_3 soak not necessary if no particulate in coil, simply rinse.
Filter Tissuequartz	4 hr.						Field blank samples will be analyzed in parallel with actual samples.
Plastic Storage Bottles			3 hr.	Rinse		X	Linear polyethylene or polypropylene.

improve the sampling accuracy. Thus, the sample probe will be positioned at the center of the duct or stack. Assemble the sampling train, so all fittings and connections are as leak free as possible. An acceptable leak rate is .03 CFM. The flowrate should be maintained at 8 liters per minute. Sample for a period of one hour or until the coils are frosted to 2/3 of their length. Temperature at the probe and filter holder must be maintained at a minimum of 288°C. Figure 5-21 is an example of an appropriate field data sheet listing the required test data.

5.6.6 Sample Recovery

Table 5-7 lists the step-by-step recovery procedure. Care must be taken to avoid introducing any dust or grease into the rinse solutions. Figure 5-22 illustrates the rinsing apparatus for the controlled condensation coil. Multiple rinses are recommended to ensure a quantitative wash of the coil. Place all solutions into properly labeled storage containers, noting liquid levels and rinse volumes. Package and ship recovered samples as to standard operating procedure.

AEROSOL SO$_3$
(CONTROLLED CONDENSATION)
FIELD DATA SHEET

Sample Location ____________________
Run # ____________________
Run Date/Time ____________________
Operator ____________________
Flowrate (cfm) ____________________
Ambient Pressure (P) ____________________

Reheater Air Flow Rate, acfm ____________________
Inlet Gas Rate, acfm ____________________
Sample Location SO$_2$ (ppm) ____________________
Boiler Load (mw) ____________________
Leak Rate ____________________

	Temperature (°F)								
			Filter				Dry Gas Meter		
Time (Min)	Stack	Probe	Skin	Out	Recirc. Water	Exit Coil	In	Out	Gas Meter Reading, cu. ft.
AVG.									

Figure 5-21. Controlled Condensation Field Data Sheet

Table 5-7. Sample Recovery

	Recovery Procedure	Storage
Probe	Probe shaken or tapped to remove loose particles then brushed.	Nalgene bottle, 20 ml
Probe Rinse	Remaining particulate matter rinsed into a separate container with acetone.	Nalgene bottle, 500 ml
Filter	Remove and place in petri dish.	Plastic
Controlled Condensation Coil CCC	Remove coil from train, invert over container and rinse repeatedly with high purity H_2O.	Nalgene bottle, 250 ml
H_2O_2 Impingers	Using known amounts of high purity H_2O, rinse all condensate from preceding lines into the impinger. Remove solution, record rinse volume and total solution volume.	Nalgene bottle, 500 ml
Na_2CO_3 Impingers	Using known amounts of high purity H_2O, rinse all condensate from preceding lines into the impinger. Remove solution, record rinse volume and total solution volume.	Nalgene bottle, 500 ml
Empty Impingers	Using known amounts of high purity H_2O, rinse all condensate from preceding lines into the impinger. Remove solution, record rinse volume and total solution volume.	Nalgene bottle, 250 ml
Blanks	Place samples of high purity H_2O, H_2O_2 and Na_2CO_3 solutions in separate containers. Return to laboratory for analysis.	Nalgene bottle, 250 ml

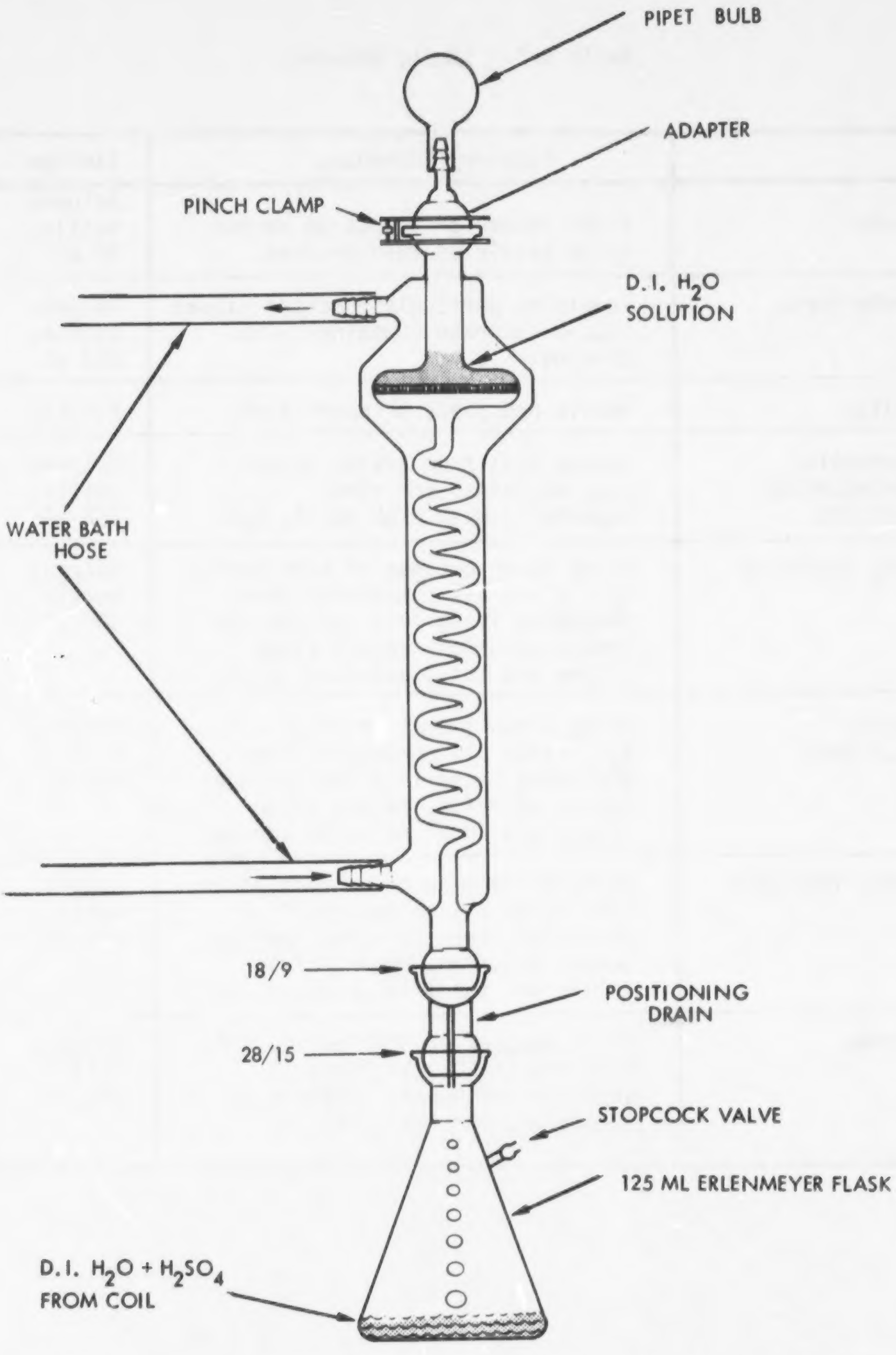
PIPET BULB
ADAPTER
PINCH CLAMP
D.I. H_2O SOLUTION
WATER BATH HOSE
18/9
POSITIONING DRAIN
28/15
STOPCOCK VALVE
125 ML ERLENMEYER FLASK
D.I. $H_2O + H_2SO_4$ FROM COIL

Figure 5-22. Controlled Condensation Coil Rinsing Apparatus

6.0 FIELD ANALYSES

6.1 INTRODUCTION

Field analyses are limited to those analyses that either: 1) are required due to significant sample degradation if delayed, or 2) simplicity dictates analysis over handling and shipping. These will include the following:

- Gas chromatographic analyses for:
  1) C1-C6 hydrocarbons
  2) Inorganic species such as CO_2, O_2, N_2, and CO
- NO_x analysis - chemiluminescence (prior to July 27, 1978)
- Water analyses
  1) Acidity
  2) Alkalinity
  3) Conductivity
  4) TSS
  5) Hardness
  6) pH
  7) Nitrate
  8) Phosphate
  9) Sulfite
  10) Sulfate
  11) Cyanide
  12) Ammonia Nitrogen
- Opacity measurements by Ringelmann and Bacharach tests

6.2 FIELD GAS CHROMATOGRAPHIC ANALYSES

6.2.1 Scope and Application

This procedure defines the Level 1 field analyses of environmental samples for:

- C1-C6 hydrocarbons, organic compounds boiling in the range 160° to 90°C.
- Inorganic compounds - CO_2, CO, O_2, N_2

Reporting Limitations. This is a survey procedure. For organic compounds, species eluting in the specified boiling point ranges are quantified as n-alkanes. This procedure is intended to give quantitative accuracy within a factor of 3.

Calibration Limitations. Quantitation based upon calibration with a gas standard is limited to the accuracy of the gas standard. Certified mixtures will be used.

Detection Limitations. The sensitivity of the flame ionization detector varies from compound to compound. However, n-alkanes as a class have a greater response than other classes. Consequently, using a n-alkane as a calibrant and assuming equal responses of all other compounds tends to give low reported values. Nominal detection limits were 1 ppm prior to March 1978 and 0.1 to 0.2 ppm after this date.

6.2.2 Summary of Method

A gas sample is analyzed in the field by gas chromatography. The instrument is set up with the column and conditions appropriate for the specific analysis to be performed. Retention time and quantitation calibrations are made with the proper standard gas mixture. Species are identified by retention times or retention time ranges and then are quantitated.

6.2.3 Definitions

- GC - Gas Chromatograph or Gas Chromatography
- NBP - Normal Boiling Point
- FID - Flame ionization detector
- TCD - Thermal conductivity detector
- RSD - Relative standard deviation

6.2.4 Sample Handling and Preservation

The samples of this analysis are contained in Tedlar bags or glass gas sampling containers. They should be analyzed as soon after acquisition as possible, preferably within two hours. Exposure to extremes of light and temperature should be avoided.

6.2.5 Apparatus

- Gas Chromatographs

  This procedure is written for use on a Shimadzu GC-Mini 1 gas chromatograph with dual flame ionization detectors and linear temperature programmer and a Shimadzu GC-3BT chromatograph with dual thermal conductivity detectors. Both GCs are also equipped with gas sampling valves. Any other equivalent instruments can be used, provided that instrument operating parameters be changed appropriately.

- Recorder

  A recorder is required. Appropriate parameters are 1 inch/min chart speed, 1 mV full scale, 1 sec full scale response time.

- Gases

  1. Helium-minimum quantity is reactor grade. A 4A or 13X molecular sieve drying tube is required. A filter should be placed between the drying tube and the instrument. The tube should be recharged after every third tank of helium.
  2. Air - "Zero" grade air is satisfactory. Air supplied by a compressor and purification train is acceptable.
  3. Hydrogen - Instrument grade is satisfactory. Hydrogen supplied by a generator is also acceptable.

- Gas Sampling Valve

  Gas samples are injected by valves. The valves may have single or dual matched loops. Dual loops should have volumes matching within 1%. Various sized loops (e.g., 1, 3, and 5 ml) should be available.

- Integrator

  An integrator is required. Peak area measurement by hand is satisfactory but too time-consuming. If manual integration is performed, the height times width at half-height method is used.

  The instrument settings made by the operator of an integrator vary with each instrument make and model and will need to be determined for the Shimadzu instruments. Typical parameters which need to be considered are the following. These should be adjusted until acceptable performance is achieved (operator judgement) and then should not be changed. These parameters should be recorded in the instrument log book.

  Noise Supression - As required
  Up-Slope Sensitivity - As required, mV/min
  Down-Slope Sensitivity - As required, mV/min
  Baseline Reset Delay - As required, min

Area Threshold - As required, V·sec
Front Shoulder Control - As required
Rear Shoulder Control - As required
Date Sampling Frequency - As required, per sec

- Columns
  1) For the inorganic gases (CO, CO_2, N_2, O_2), the following columns are needed: (a) 5 ft x 1/8 in., stainless steel, packed with Chromosorb 102, (b) 8 ft x 1/8 in., stainless steel, packed with 13X molecular sieve, and (c) 5 ft x 1/8 in., steel, empty.
  2) For the C1-C6 hydrocarbons, a 6 ft x 1/8 in., stainless steel column packed with Poropak Q is required. If temperature programming is required, dual and matched columns are necessary.

6.2.6 Reagents

- Gas standard - C1 to C6 n-alkanes in nitrogen. Concentrations may range from 5-100 ppm. The standard must be certified.
- Gas standard - inorganic gases CO, CO_2, O_2 in N_2. This standard must be certified.

6.2.7 Procedure - C1 to C6 Analysis

During van set-up at each new test site, the GCs will be fully calibrated as described below. Partial calibrations will be performed as required, specified, or directed by the test director.

Setup and Checkup. Each day the operator will verify the following:

1. All gas supplies are adequate and at the proper pressures.
2. Verify carrier gas flow rate is 30 ± 2 ml/min. Flow rate is checked at analytical column outlet after disconnection from the instrument. The instrument must be at room temperature.
3. Verify hydrogen flow rate is 30 ± 2 ml/min. Flow rate is checked at the gas control panel on the GC. This flow rate may change with other instruments.
4. Verify air flow is 300 ± 20 ml/min. Air flow rate is checked at the gas control panel on the GC.
5. Verify the electrometer is functioning properly. The electrometer will be balanced and the bucking controls will be set as required.

6. Verify integrator and recorder are functioning properly.
7. Obtain a list of samples to be analyzed.

Calibration. To obtain the temperature ranges for reporting the results of the C1-C6 GC analyses, the chromatograph is given a normal boiling point-retention time calibration. The n-alkanes, their normal boiling points (NBP), and data reporting ranges are given below.

	NBP, °C	Reporting Range, °C	Report As
Methane	-161	-160 to -100	C1
Ethane	-88	-100 to -50	C2
Propane	-42	-50 to 0	C3
Butane	0	0 to 30	C4
Pentane	36	30 to 60	C5
Hexane	69	60 to 90	C6

- Apparatus

The required apparatus is specified below.

1. GC-Mini 1, recorder, and integrator set up according to manufacturer's manual and performance-checked.
2. Standard mixture as specified in Section 6.2.6.
3. Conditions: Injector temperature ______; detector temperature ______; oven temperature, isothermal at ______°C or programmed from ______°C to ______°C at ______°C/min.

- Initial Calibration Procedure

Connect the C_1-C_6 standard gas bottle to the sampling valve, and flow the gas through the valve at a constant, low and reproducible flow rate of 20 std. ml/min measured at the sample valve outlet using a soap bubble flowmeter. When the sample valve is sufficiently purged, actuate the valve and inject the contents of the sample loop into the chromatograph. Simultaneously, start the integrator and temperature programmer (if it is used). Obtain the chromatograms and the integrator output. Retention times and responses shall agree to within 5% relative standard deviation. If any doubt exists concerning the relationship between the real sample GC peaks and those obtained from calibration, a small aliquot of the calibration gas should be spiked with the sample in order to verify retention times.

- Daily Calibration Check

  The C_1-C_6 standard gas mixture will be injected and analyzed at the start of each day. The retention times and responses for each component should agree with the initial calibration data to within ±10% relative. The full calibration need not be repeated.

- Analysis of Samples

  1. Chromatograph, recorder, and integrator set up according to the manufacturer's manuals, calibrated, and confirmed operating parameters. Parameters are to be listed on each chromatogram.
  2. Conditions: Column temperature, 100°C, electrometer, 1×10^{-10} A/mV; recorder, 1 inch/min and 1 mV full scale.
  3. Label recorder chart: sample number, date, etc.
  4. Connect sample bag to gas sample valve, purge the sample loop with the sample and then inject the contents of the loop.
  5. Start integrator and recorder.
  6. When analysis is finished, give chromatogram and integrator output to data analyst.

6.2.8 Calculations - C1 to C6 Hydrocarbons

Boiling Point - Retention Time Calibration

The calibration curve is constructed in the following manner:

1. For each alkane, calculate the average retention time and relative standard deviation.
2. Plot the normal boiling points of the alkanes versus the average retention times (in seconds).
3. Draw in the curve.
4. On the curve, locate and record the retention times corresponding to the reporting ranges: -160° to -100°, -100° to -50°, -50° to 0°, 0° to 30°, 30° to 60°, and 60° to 90°C.

Quantitation Calibration

The required data for this calibration are on the data sheet. The calibration and quantitation are effected in the following manner:

1. Calculate the average area responses and relative standard deviations for the propane calibrant.
2. Plot response ($\mu V \cdot sec$) as ordinates versus the concentration of the standard in mg/m^3 injected, as abscissae. Draw in curve. Perform least squares linear regression and obtain the slope ($\mu V \cdot sec \cdot m^3/mg$).

Quantitation - Analyses

The required data are on the data sheet. The quantitation is effected in the following manner:

1. In each retention time range, sum up the peak areas.
2. Convert peak areas ($\mu V \cdot sec$) to mg/m^3 by dividing by the proper response (slope factor).
3. Record the total concentration of material in each retention time range on the data sheet.

6.2.9 Procedure - Inorganic Gases

During van setup at each new test site, the GCs will be fully calibrated as described below. Partial calibrations will be performed as specified below and/or as directed by the Test Director.

Setup and Checkout. Each day the operator will verify that:

1. The carrier gas supply is adequate and at the proper pressure.
2. The carrier gas flow rate (nitrogen) is 30 ± 2 ml/min. The flow rate is checked at the column outlet. The column must be at room temperature.
3. The detector is set and working properly.
4. The recorder and integrator are working properly.
5. Obtain a list of samples to be analyzed.

Calibration. Connect the inorganic standard gas bottle to the gas sampling valve, and flow the gas through the valve at a constant and reproducible flow rate of 20 std. ml/min, measured at the sample valve outlet with a soap bubble flow meter. When the valve is sufficiently purged, actuate the valve, and inject the contents of the sample loop into the chromograph. Simultaneously, start the integrator. When the CO_2

peak has eluted, switch the detector polarity and obtain the remaining peaks. The retention times and peak areas will agree to within 5% relative standard deviation.

The inorganic standard gas mixture will be injected and analyzed at the start of each day. The retention times and responses of each component will agree with the initial site calibration data to within ±10%.

Analysis of Samples

1. Chromatograph, recorder, and integrator setup according to manufacturer's manuals, calibrated, and confirmed operating parameters. Parameters are to be listed on each chromatogram.
2. Conditions
   - Carrier flow rate: 30 ± 2 ml/mv
   - Bridge current: 100 mA
   - Detector temperature: $100^{\circ}C$
   - Oven temperature: $45^{\circ}C$
   - Attentuator: as required
   - Recorder: 1mV full scale, 1 inch/min
   - Integrator: as required
3. Label the recorder chart with sample number, date, and operating parameters.
4. Connect the gas sampling container to the gas sampling valve. Purge the sample loop with the sample. Inject the sample.
5. Simultaneously, start the integrator and recorder.
6. When the analysis is finished, give the chromatogram and integrator output to the data analyst.

6.2.10 Calculations - Inorganic Gases

The required data for these analyses are on the data sheet.

Calibration

1. Calculate average and standard deviation of the retention time and response for each component in the chromatograms of the standard.
2. Plot response ($\mu V \cdot sec$) as ordinates versus the concentration of each component (mg/m^3) injected as abscissae. Draw in the curves. Perform least squares linear

regressions for each component, and obtain the slopes ($\mu V \cdot sec \cdot m^3/mg$).

Analyses

The required data are on the data sheet. Data reduction is effected as follows:

1. Components (CO, CO_2, O_2, N_2) are identified by retention time comparison with the standard chromatograms. (Flow rate reproducibility is critical.)
2. Divide the areas found in the sample chromatogram by the appropriate slope and obtain the concentration of each component in mg/m^3.

6.2.11 Checking the Gas Sample Valve for Cleanliness

Periodically, the gas sampling valve should be checked to determine if it is contributing contamination to the analysis of samples. Pass the helium carrier through the sample loops then inject their contents and analyze as if it were a sample. If significant peaks are noted, the valve should be cleaned per the manufacturer's instructions.

6.2.12 Precision and Accuracy

An error propagation analysis is beyond the scope of this procedure. With reasonable care, peak area reproducibility of a standard should be of the order of 1% relative standard deviation (RSD). The RSD of the sum of all peaks in a fairly complex sample might be of the order of 5%-10%. Accuracy is more difficult to assess. With good analytical technique, accuracy and precision should be of the order of 10%-20%.

Since both standards and samples are injected at ambient pressure, calibration curves will vary from site-to-site with variations in ambient pressure. If ambient pressure is noted at the start of each analysis, data can be corrected to a common pressure for better comparison.

6.3 NO_x ANALYSIS - CHEMILUMINESCENCE MEASUREMENT ON GAS BAG SAMPLE

6.3.1 Scope and Applications*

Method is applicable to the determination of NO/NO_2 in all gas samples, including samples collected in the integrated gas sampling train using Tedlar bags. The method is suitable for detection of NO/NO_x in the 0-2,500 ppm range. Sensitivity is approximately 1 ppb.

6.3.2 Summary of Method

NO and O_3 react ($NO + O_3 \rightleftarrows NO_2 + O_2 + h\nu$) and emit light at 0.6 - 3μ. A high sensitivity photomultiplier monitors the light emitted in the reaction chamber of the chemiluminescence instrument. NO_x is determined in the same fashion after NO_2 is reduced to NO in a catalytic converter.

6.3.3 Interferences

Water and ammonia may interfere with the analyses. The manufacturer's manual should be consulted for recommendations on avoiding these interferences.

6.3.4 Apparatus

Chemiluminescence instrument.

6.3.5 Reagents

No reagents are required for this analysis.

6.3.6 Procedure

The analysis procedure using the chemiluminescence instrument is straightforward and simply requires the introduction of the sample into the sampling port. The primary consideration for chemiluminescence analysis involves calibration of the instrument, which must be performed on a daily basis. This procedure can be conducted using manufacturer specifications.

6.3.7 Accuracy and Precision

Data are unavailable on the precision and accuracy attainable with the procedure.

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*This method was utilized prior to July 27, 1978.

6.4 NO_x ANALYSIS - EPA METHOD 7

This method was adopted for use after July 27, 1978 because it was found that there was significant deterioration of NO_x in the gas bag which caused results to be low. Although these results were usually within a factor of 2, much higher accuracy is required in order that the data for this criteria pollutant be useful.

6.4.1 Scope and Application

This method is applicable to the determination of NO/NO_2 in all stack gas samples in most concentrations expected in the program up to 3000 ppm. Method 7 may not provide accurate results at NO_x concentrations below 200 ppm.

6.4.2 Summary of Method

A special sample of stack gas is drawn into a specially designed glass vessel which contains an oxidizing solution. NO_x is absorbed into the solution and converted into nitrate which is determined.

6.4.3 Interferences

SO_2 will interfere with this analysis if care is not taken to absorb all of the gas into the oxidizing solution as soon as possible. This is done by vigorously shaking the sample vessel immediately after the sample is taken.

6.4.4 Apparatus, Reagents, and Procedure

The detailed Method 7 procedure is reproduced from the Federal Register in Appendix C.

6.5 WATER ANALYSIS

To facilitate the analysis of simple water quality parameters and to provide for a most cost effective method to acquire appropriate source data, the Hach analysis kit DR-EL/2 model will be utilized in the field for a Level 1 water analysis effort. Parameters to be analyzed by the Hach Kit include pH, acidity or alkalinity, conductivity, hardness, TSS, NO_3^-, $PO_4^{\equiv}$, $SO_3^{=}$, $SO_4^{=}$, CN^- and NH_3-N. The following is a discussion of the methodologies utilized for these analyses. For a complete water analysis sampling and analysis plan, see Section 3.8. Sample data sheets, Figures 6-1 to 6-5, are at the end of this Section.

6.5.1 Acidity

6.5.1.1 Scope and Application

This method is applicable to surface waters, sewage and industrial wastes, particularly mine drainage and receiving streams, and other waters containing slowly hydrolyzable materials in sufficient concentration to significantly delay attainment of equilibrium at the titration end point. The method covers the range from approximately 10 mg/liter acidity to approximately 1000 mg/liter as $CaCO_3$, using a 50 ml sample.

6.5.1.2 Summary of Method

Two titrations are performed on each sample with standard alkali to designated pH levels, with the end points determined by the color change of added indicators. To measure the acidity resulting from oxidation, hydrolysis or similar reactions of species in the water, one sample aliquot is boiled to accelerate and complete these reactions prior to the titration.

6.5.1.3 Definitions

This method measures the mineral acidity of a sample plus the acidity resulting from oxidation and hydrolysis of polyvalent cations, including salts of iron and aluminum.

6.5.1.4 Interferences

Natural color on the formation of a precipitate while titrating the sample may mask the color change of the indicators. Oxidizing and reducing species and some industrial waste water components may also interfere with the color change producing reactions of the indicators. Volatile components contributing to the sample acidity may be lost when the sample is boiled, thus introducing some degree of error.

6.5.1.5 Apparatus

- Erlenmeyer flasks, 50 ml, well rinsed with deionized water
- Pipets, graduated with capacity greater than 12 ml
- Hot plate

6.5.1.6 Reagents

- Sodium hydroxide standard solution 0.02N
- Brom Cresol Green-Methyl Red Indicator Solution (Hach catalog number 451-36)
- Phenolphthalein indicator solution, 1 g/l

6.5.1.7 Procedure for Methyl Orange Acidity

1) Pipet 11.4 ml of the water sample into the 50-ml Erlenmeyer flask.
2) Add 2 drops of brom cresol green-methyl red indicator solution and swirl to mix. If the sample turns green, the methyl orange acidity is zero. If the sample turns pink, proceed with Step 3.
3) Titrate the sample with sodium hydroxide standard solution, 0.0227N, while constantly swirling the flask, until the color changes from pink to the first shade of blue-gray.

6.5.1.8 Procedure for Phenolphthalein Acidity

1) Pipet 11.4 ml of the water sample into the 50-ml erlenmeyer flask.
2) Add 2 drops of phenolphthalein indicator solution and swirl to mix.
3) Boil the sample for 2 minutes.
4) If the sample turns pink with the addition of the phenolphthalein and remains pink after boiling, the phenolphthalein acidity is zero. If the sample remains colorless with the addition of the phenolphthalein or turns pink initially and the color fades during boiling, proceed with Step 5.
5) Titrate the hot sample with sodium hydroxide standard solution, 0.0227N, while continuously swirling the flask, until a pink color appears.

6.5.1.9 Calculations

Methyl orange acidity, as mg/l $CaCO_3$ = $100 \times V_1 \times N$

where V_1 = volume of standard alkali used in titration to brom cresol green-methyl red end point

N = normality of standard alkali

Phenolphtalein acidity, as mg/l $CaCO_3$ = $100 \times V_2 \times N$

where V_2 = volume of standard alkali used in titration to phenolphthalein end point

N = normality of standard alkali

6.5.1.10 Precision

On a round robin conducted by ASTM on 4 acid mine waters, including concentrations up to 2000 mg/liter, the precision was found to ±10 mg/liter.

6.5.2 Alkalinity

6.5.2.1 Scope and Application

This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes. The method is suitable for all concentration ranges of alkalinity; however, appropriate aliquots should be used to avoid a titration volume greater than 50 ml. Automated titrimetric analysis is equivalent. The sample must be analyzed as soon as practical; preferably, within a few hours. Do not open sample bottle before analyses. Substances, such as salts of weak organic and inorganic acids present in large amounts, may cause interference in the electrometric pH measurements. Oil and grease, by coating the pH electrode, may also interfere, causing sluggish response.

6.5.2.2 Summary of Method

An unaltered sample is titrated to an electrometrically determined end point of pH 4.5. The sample must not be filtered, diluted, concentrated, or altered in any way.

6.5.2.3 Reagents

The following reagents are obtained from HACH.

Cat. No.	Description
● 203-14	Sulfuric Acid Standard Solution, 0.020N
● 451-36	Brom Cresol Green-Methyl Red Indicator Solution
● 1897-36	Phenolphthalein Indicator Solution, 1g/liter

6.5.2.4 Procedure

1) Pipet 10.0 ml of the water sample into the 50-ml Erlenmeyer flask. See Note A.
2) Add one drop Phenolphthalein Indicator Solution and swirl to mix.
3) If the sample turns pink, titrate with Sulfuric Acid Standard Solution, 0.020N, to a colorless end point. Record volume. If the pink color does not develop, proceed with Step 5.
4) Multiply the number of ml of Sulfuric Acid Standard Solution 0.020N, used in Step 3 by 100 to obtain the mg/liter pheonolphthalein alkalinity (as $CaCO_3$). See Note B.
5) Add 2 drops of Brom Cresol Green-Methyl Red Indicator Solution and swirl to mix.

6) Continue the titration with Sulfuric Acid Standard Solution 0.020N, until the color changes from green or blue-green to pink. Record volume.

7) Multiply the number of ml of Sulfuric Acid Standard Solution 0.020N, used in both tests by 100 to obtain the mg/liter total alkalinity (as $CaCO_3$). See Note B.

TABLE 6-1. Alkalinity Relationship

Result of Titration	Hydroxide Alkalinity	Carbonate Alkalinity	Bicarbonate Alkalinity
Phenolphthalein Alkalinity = 0	0	0	Equal to total
Phenolphthalein Alkalinity less than half of Total Alkalinity	0	2 times the Phenolphthalein Alkalinity	Total Alkalinity minus two times Phenolphthalein Alkalinity
Phenolphthalein Alkalinity equal to half of Total Alkalinity	0	2 times the Phenolphthalein Alkalinity	0
Phenolphthalein Alkalinity greater than one half of Total Alkalinity	2 times the Phenolphthalein minus Total Alkalinity	2 times the difference between Total and Phenolphthalein Alkalinity	0
Phenolphthalein Alkalinity equal to Total Alkalinity	Equal to the Total Alkalinity	0	0

Notes

A. The 50 ml Erlenmeyer flask should be rinsed with demineralized water three or more times before each test.

B. The mg/liter hydroxide, carbonate, and bicarbonate alkalinities (as $CaCO_3$) can be calculated from the Table 6-1, Alkalinity Relationship.

6.5.2.5 Precision and Accuracy

Forty analysts in seventeen laboratories analyzed synthetic water samples containing increments of bicarbonate, with the following results:

Increment as Alkalinity mg/liter, $CaCO_3$	Precision as Standard Deviation mg/liter, $CaCO_3$	Accuracy as	
		Bias, %	Bias mg/liter $CaCO_3$
8	1.27	+10.61	+0.85
9	1.14	+22.29	+2.0
113	5.28	- 8.19	-9.3
119	5.36	- 7.42	-8.8

In a single laboratory using surface water samples at an average concentration of 122 mg $CaCO_3$/liter the standard deviation was ±3.

FIGURE 6-2. Data Sheet - Alkalinity

SAMPLE LOCATION ______________ DATE SAMPLE REC'D ______________

SAMPLE MEDIUM ______________ DATE SAMPLE ANALYZED ______________

LOG NUMBER ______________ ANALYZED BY ______________

VERIFIED BY ______________

I

	STANDARD REAGENTS USED	REFERENCE METHOD	DATE REAGENT STANDARDIZED
1.			
2.			
3.			
4.			

II CALCULATIONS

TOTAL ALKALINITY

$$\text{As mg/liter CaCO}_3 = \frac{V_{acid} \times N_{acid} \times 50{,}000}{V_{sample}} = 20^* \text{ Vacid}$$

* Valid when Nacid = 0.02 N, and Vsample = 50 ml

III SPECIFIC COMMENTS ON SAMPLE CHARACTERISTICS

VISUAL ______________________________

ODOR ______________________________

COLOR ______________________________

SPECIFIC COMMENTS ON SAMPLE ANALYSIS ______________________________

VISUAL ______________________________

ODOR ______________________________

ERRORS OBSERVED ______________________________

6.5.3 Specific Conductance

6.5.3.1 Scope and Application

The method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

6.5.3.2 Summary of Method

The specific conductance of a sample is measured by use of a self-contained conductivity meter, Wheatstone bridge-type, or equivalent.

Samples are preferably analyzed at 25°C. If not, temperature corrections are made and results reported at 25°C.

6.5.3.3 Definition

Conductivity measures the ability of a water sample to carry an electric current. This depends on the total concentration of ionizable species dissolved in the water and the temperature at which the measurement is made.

6.5.3.4 Sample Handling and Preservation

Representative samples shall be taken in distilled water rinsed glassware.

Since delayed analysis of sample may cause CO_2 absorption and subsequently change the conductivity value, determination will be made as soon as possible.

6.5.3.5 Apparatus

Self-contained conductance instrument; a thermometer capable of reading to the nearest 0.1°C, conductivity cell.

6.5.3.6 Reagents

- Distilled water with conductivity less than 1 µmhos/cm
- Standard potassium chloride 0.0100 M

6.5.3.7 Procedure

1. Insert the Conductivity Meter Scale in the meter and set the RANGE switch to 5.
2. Connect the probe assembly to the five-pin receptacle on the spectrophotometer panel.
3. Immerse the probe in a beaker containing the sample or standard solution. The depth of the solution must be sufficient to allow the probe to be immersed to the vent holes.

4. Select the appropriate range, beginning with the highest range and working down. Each range on the meter scale is numbered to correspond with the switch position numbers. If the reading is in the lowest 10 percent of the range, switch to the next lower range. Take the reading and record. See Notes A and B.

   Notes:

   A. Additional conductivity meter scales have been included as part of the conductivity option to provide equivalent readings in ohms/cm, mg/liter sodium chloride and gr/gal sodium chloride. Keep in mind that the sodium chloride calibrations are based on pure NaCl solutions. Readings taken from these scales should only be considered as representing the concentration of sodium chloride which is a conductivity equivalent to the conductivity of the sample solution and does not necessarily represent the actual concentration of sodium chloride in the sample.

   B. Water samples containing oils, greases, or fats will coat the electrodes and affect the accuracy of the readings. Should this occur, the probe should be cleaned with a strong detergent solution or dipped in a one-to-one mixture of hydrochloric acid and distilled water and then thoroughly rinsed with distilled water.

6.5.3.8 Comments

Instrument must be standarized with KCl solution before daily use. Conductivity cell must be kept clean.

6.5.3.9 Precision and Accuracy

Forty-one analysts in 17 laboratories analyzed six synthetic water samples containing increments of inorganic salts, with the follwoing results:

Increment as Specific Conductance μmhos/cm	Precision as Standard Deviation μ mhos/cm	Accuracy as Bias, %	Accuracy as Bias, μ mhos/cm
100	7.55	-2.02	-2.0
106	8.14	-0.76	-0.8
808	66.1	-3.63	-29.3
848	79.6	-4.54	-38.5
1640	106	-5.36	-87.9
1710	119	-5.08	-86.9

In a single laboratory (MDQARL), using surface water samples with an average conductivity of 536 μmhos/cm at 25°C, the standard deviation was ±6.

6.5.4 Total Suspended Solids (TSS)

6.5.4.1 Scope and Application

Method is applicable to drinking, surface, and saline waters, domestic and industrial wastes. The practical range of determinations is 0-500 mg/l; this range can be extended by sample dilution.

6.5.4.2 Summary of Method

The sample is prepared by homogenizing it in a high speed blender, and the turbidity is determined using the Hach Test Kit spectrophotometer.

6.5.4.3 Interferences

Gas bubbles in the sample must be removed by swirling or by addition of tap water.

6.5.4.4 Apparatus

- Graduated Cylinder, 500 ml
- Glass Stirring Rod
- Blank Meter Scale for Hach Test Kit
- Serological Pipet
- Pipet Filter
- Blender

6.5.4.5 Reagents

- Tap water

6.5.4.6 Procedure*

1. Fill a sample cell to the 25 mark with tap water and place it in the cell holder. Insert the Suspended Solids Meter Scale in the meter and adjust the Wavelength Dial to the end of travel at the infrared (IR) end of the scale. Adjust the LIGHT CONTROL for a meter reading of zero mg/l.
2. Take a water sample by filling a clean 500-ml graduated cylinder to the 500-ml mark. Pour the sample into the container of a blender. See Note A.
3. Blend at high speed for exactly two minutes.
4. Pipet 25 ml of the sample from the center of the blender container into a clean sample cell.

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* Adapted from Hach Direct Reading Engineers Laboratory Methods Manual (DR-EL/2).

5. Check the meter reading to be sure the zero mg/l setting has not varied.
6. Swirl the sample cell containing the prepared sample, place it in the cell holder, and read the mg/l suspended solids. See Note B.

Notes:

A. A Waring blender or equivalent is suggested for use in this step. Equipment of this type is generally available from hardware stores or applicance centers.

B. The meter scale has been calibrated using samples from two municipal sewage treatment plants, one a trickling filter and the other an activiated sludge unit. Simultaneous samples were run using the photometric method and the membrane filter technique. For greater accuracy, a blank meter scale can be calibrated to a specific sample by simultaneous comparison with the membrane filter method.

6.5.4.7 Calculations

Mg/l of suspended solids are read directly from the spectrophotometer.

6.5.4.8 Precision and Accuracy

Data are unavailable on the precision and accuracy of the method.

6.5.5 Hardness

6.5.5.1 Scope and Application

This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes. The method is suitable for all concentration ranges of hardness; however, in order to avoid large titration volumes, use a sample aliquot containing not more than 25 mg $CaCO_3$.

Excessive amounts of heavy metals can interfere. This is usually overcome by complexing the metals with cyanide.

Routine addition of sodium cyanide solution (Caution: deadly poison) to prevent potential metallic interference is recommended.

6.5.5.2 Summary of Method

Calcium and magnesium ions in the sample are sequestered upon the addition of disodium ethylenediamine tetraacetate (Na_2EDTA). The end point of the reaction is detected by means of Calmagite Indicator, which has a red color in the presence of calcium and magnesium and a blue color when the cations are sequestered.

6.5.5.3 Reagents

The following reagents are obtained from Hach.

Cat. No.	Description
• 205-14	Titra Ver Hardness Titrant
• 424-13	Buffer Solution
• 928-99	Man Ver II Hardness Indicator Powder Pillow

6.5.5.4 Procedure

1. Pipet 10.0 ml of the water sample into a 50-ml Erlenmeyer flask.
2. Add 3 drops of Buffer Solution and swirl to mix.
3. Add the contents of one ManVer II Hardness Indicator Powder Pillow and swirl to mix.
4. While constantly swirling the flask, titrate the sample with Titra Ver Hardness Titrant until the color changes from red to pure blue. See Note A.
5. Multiply the number of ml of TitraVer Hardness Titrant used by 100 to obtain the mg/liter total hardness (as $CaCO_3$). See Note B.

Notes:

A. Titrate slowly towards the end point to allow time for the reaction and color change to take place.

B. The presence of copper and/or iron may cause the end point to be masked or delayed. These interferences can be overcome by adding a 0.2-gram scoop of Potassium Cyanide after Step 2.

6.5.5.5 Precision and Accuracy

Forty-three analysts in nineteen laboratories analyzed six synthetic water samples containing exact increments of calcium and magnesium salts, with the following results:

Increment as Total Hardness mg/liter, $CaCO_3$	Precision as Standard Deviation mg/liter, $CaCo_3$	Accuracy as	
		Bias %	Bias mg/liter, $CaCO_3$
31	2.87	-0.87	-0.003
33	2.52	-0.73	-0.24
182	4.87	-0.19	-0.4
194	2.98	-1.04	-2.0
417	9.65	-3.35	-13.0
444	8.73	-3.23	-14.3

In a single laboratory (MDQARL), using surface water samples at an average concentration of 194 mg $CaCO_3$/liter the standard deviation was ± 3.

6.5.6 pH

6.5.6.1 Scope and Application

This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

6.5.6.2 Summary of Method

The pH of a sample is an electrometric measurement, using either a glass electrode in combination with a reference potential (saturated calomel electrode) or a combination electrode (glass and reference).

6.5.6.3 Comments

- The sample must be analyzed as soon as practical; preferably within a few hours. Do not open sample bottle before analysis.
- Oils and greases, by coating the pH electrode, may interfere by causing sluggish response.
- At least three buffer solutions must be used to initially standardize the instrument. They should cover the pH range of the samples to be measured.

6.5.6.4 Precision and Accuracy

Forty-four analysts in twenty laboratories analyzed six synthetic water samples containing exact increments of hydrogen-hydroxyl ions, with the following results:

Increment as pH Units	Precision as Standard Deviation pH Units	Accuracy as	
		Bias, %	Bias pH Units
3.5	0.10	-0.29	-0.01
3.5	0.11	-0.00	
7.1	0.20	+1.01	+0.07
7.2	0.18	-0.03	-0.002
8.0	0.13	-0.12	-0.01
8.0	0.12	+0.16	+0.01

In a single laboratory (MDQARL), using surface water samples at an average pH of 7.7, the standard deviation was ±0.1.

6.5.7 Nitrate Nitrogen

6.5.7.1 Scope and Application

Method is applicable to drinking, surface and saline waters, domestic and industrial wastes. Modification can be made to remove or correct for turbidity, color, salinity, or dissolved organic compounds in the sample. The applicable range is 0-30 mg/l, although this range can be extended with suitable dilution.

6.5.7.2 Summary of Method

The sample is reacted with Hach NitraVer V Nitrate Reagent which consists of a reducing agent, such as granulated copper-cadmium, plus a diazotization agent (sulfanilamide) and a coupling agent N-(1-naphthyl) - ethylenediamine dihydrochloride. This forms a highly colored azo dye which is measured spectrophotometrically at 500 nm. The method is also known as the cadmium reduction method.

6.5.7.3 Interferences

Interferences from nitrite ion can be eliminated by adding bromine water dropwise to the sample until the yellow color of bromine persists, followed by addition of one drop of phenol solution to destroy the color (see Reagents, Section 6.5.7.5). Strong oxidizing and reducing substances will also interfere. Ferric iron causes high results and must not be present. Large amounts of chloride cause low results.

6.5.7.4 Apparatus

Hach Portable Test Kit Spectrophotometer for use at 500 nm, providing a light path of 1 cm or longer. Standard laboratory glassware, including an eye dropper.

6.5.7.5 Reagents

- Hach NitraVer V Nitrate Reagent Powder Pillows
- Nitrate Nitrogen Standard Solution, 10 mg/liter as N
- Phenol Solution, 3 percent
- Bromine Water

6.5.7.6 Procedure*

1. Fill a clean sample cell with sample to the 25 mark. See Notes A and B.

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* Abstracted from Hach Direct Reading Engineers Laboratory Methods Manual (DR-EL/2)

2. Add the contents of one NitraVer V Nitrate Reagent Powder Pillow to the sample cell, stopper, and shake vigorously for exactly one minute. See Notes C and D. An amber color will develop if nitrate nitrogen is present. To allow time for proper color development, wait at least 5 minutes but not more than 15 minutes before completing Steps 3 and 4.
3. Fill another sample cell to the 25 mark with some of the original water sample and place it in the cell holder. Insert the Nitrogen, Nitrate (NitraVer V Method) Meter Scale in the meter and adjust the Wavelength Dial to 500 nm. Adjust the LIGHT CONTROL for a meter reading of zero mg/l.
4. Place the prepared sample in the cell holder and read the mg/l nitrate nitrogen (N). See Notes E and F.

Notes:

A. The sample cells and stoppers should be rinsed by shaking with portions of demineralized water several times before each test.

B. NitraVer V Nitrate Reagent is slightly temperature sensitive. For best results, the test should be performed with a sample temperature of 20° to 24°C (68° to 75°F).

C. A deposit of unoxidized metal and drying agent will remain after the NitraVer V Nitrate Reagent Powder has dissolved. This will have no effect on test results.

D. The extent of color development in the nitrate nitrogen test using NitraVer V Nitrate Reagent Powder is partially affected by the shaking time and technique of the analyst. For most accurate results, the analyst should make successive tests on a solution containing a known amount of nitrate and adjust his or her shaking time to obtain the most accurate results.

E. The results can be expressed as mg/l nitrate (NO_3) by multiplying the mg/l nitrate nitrogen (N) and 4.4.

F. The reagent blank must be determined on each new lot of NitraVer V Nitrate Reagent by running the test using demineralized water in Steps 1 and 3. The value of the blank must then be subtracted from the final reading for each sample tested with that reagent lot. An occasional check should also be made between purchases to determine the condition of the NitraVer V Nitrate Reagent.

6.5.7.7 Calculations

The concentration of nitrate nitrogen in mg/l is read directly from the instrument. As indicated in Note E above, this concentration can be converted to mg/liter (NO_3) by multiplying the mg/liter nitrate nitrogen (N) concentration by 4.4.

6.5.7.8 Precision and Accuracy

Three laboratories analyzed four natural water samples containing exact increments of inorganic nitrate, with the following results:

Increment as Nitrate Nitrogen mg N/liter	Precision as Standard Deviation mg N/liter	Accuracy As	
		Bias, %	Bias, mg N/liter
0.29	0.012	+ 5.75	+0.017
0.35	0.092	+18.10	+0.063
2.31	0.318	+ 4.47	+0.103
2.48	0.176	- 2.69	-0.067

6.5.8 Phosphate, Total Organic and Inorganic

6.5.8.1 Scope and Application

Method is applicable to drinking, surface and saline waters, domestic and industrial wastes. It may also be applicable to sediment-type samples, sludges, algal blooms, etc. The range of application is 0-2 mg/liter.

6.5.8.2 Summary of Method

Total organic and inorganic phosphate are determined by oxidation of the phosphorous forms present in the sample to orthophosphate using potassium persulfate. The orthophosphate present is then treated with Hach PhosVer III Phosphate Reagent Powder Pillow (ammonium molybdate and antimony potassium tartrate in an acidic medium) to form an antimony-phosphomolybdate complex, which is subsequently reduced to an intensely blue-colored complex (by ascorbic acid) and measured spectrophotometrically at 700 nm.

6.5.8.3 Interferences

The following interfere above the concentrations listed: copper, 10 mg/l; iron, 50 mg/l; silica, 50 mg/l; and silicate, 10 mg/l. Arsenate and hydrogen sulfide also interfere.

6.5.8.4 Apparatus

Hach Portable Test Kit Spectrophotometer for use at 700 nm. Standard laboratory glassware.

6.5.8.5 Reagents

- Sulfuric acid solution, 5.25N
- Hach Potassium Persulfate Powder Pillow
- Solium hydroxide, 5.0N
- Hach PhosVer III Phosphate Reagent Powder Pillow
- Sterno, 2-5/8 oz cans.
- Demineralized Water
- Filtration Aid Solution

6.5.8.6 Procedure*

1. Fill a clean 25-ml graduated cylinder with sample to the 25-ml mark. Pour the sample into a clean 50-ml Erlenmeyer flask. See Note A.
2. Add the contents of one Potassium Persulfate Powder Pillow and swirl to mix.
3. Add 2 ml of 5.25N Sulfuric Acid Standard Solution using the 1.0 ml calibrated dropper and swirl to mix.
4. Place the flask on a hot plate or over a flame (Sterno provided) and boil gently for 30 minutes, maintaining the sample volume near the 20-ml mark with demineralized water. See Note B. Do not allow the volume to exceed 20 ml toward the end of the 30-minute period and do not boil to dryness. Allow the sample to cool before proceeding.
5. Add 2 ml of 5.0N Sodium Hydroxide Standard Solution using the 1.0 ml calibrated dropper and swirl to mix.

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* Abstracted from Hach Direct Reading Engineers Laboratory Methods Manual (DR-EL/2)

6. Return the sample to the graduated cylinder. Bring the volume to 25 ml by rinsing the flask with small portions of demineralized water and using the rinse water to correct the volume.
7. Take sample from (6) by filling a clean sample cell to the 25 mark. See Note C.
8. Add the contents of one PhosVer III Phosphate Reagent Powder Pillow and swirl to mix. See Note D. A Blue-violet color will develop if phosphate is present. Allow at least 2 minutes, but not more than 10 minutes, for the color to fully develop before completing Steps 3 and 4.
9. Fill another sample cell to the 25 mark with some of the original water sample and place it in the cell holder. Insert the Phosphate (PhosVer III Method) Meter Scale in the meter and adjust the Wavelength Dial to 700 nm. Adjust the LIGHT CONTROL for a meter reading of zero mg/l.
10. Place the prepared sample in the cell holder and read the mg/l total phosphate (PO_4). See Note E.
11. To determine inorganic phosphate only, repeat Steps 1 through 10 above, but omit Step 2. Read the results as mg/l total inorganic phosphate.
12. The mg/l of organic phosphate can be determined by subtracting the amount of total inorganic phosphate (Step 11) from the results of the total phosphate test (Step 10).

Notes:

A. If the sample is turbid or colored the procedure must be run using a 50-ml sample, 2 Potassium Persulfate Pillows and 4 ml each of Sulfuric Acid and Sodium Hydroxide Standard Solutions with a 50-ml graduated cylinder and a 125-ml Erlenmeyer flask. Use 25 ml of the oxidized sample to zero the instrument in Step 9. This will compensate for any turbidity or color which is destroyed during the oxidation. If the sample is highly turbid it may be necessary to carry out the filtration procedure described in Note C before the hydrolysis of a 25 ml sample of the filtrate.

B. The 30-minute digestion procedure can be more easily accomplished by using a "double boiler" technique. Place the flask containing the sample in a small pan or beaker filled with enough water to bring its level above the level of the sample in the flask. Heat the water to boiling and continue heating until the sample in the flask has boiled for 30 minutes. This technique assures even heating of the sample and helps prevent boiling to dryness.

C. Large amounts of turbidity may cause inconsistent results in the phosphate tests because the acid present in the powder pillow may dissolve some of the suspended particles and because of variable desorption of orthophosphate from the particles. The following pretreatment is recommended for highly turbid samples although it will result in the loss of any suspended orthophosphate which may be present.

   1. Take a water sample by filling a clean 100-ml graduated cylinder to the 100-ml mark. Pour the sample into a clean 125-ml Erlenmeyer flask.
   2. Add 5 drops of Filtration Aid Solution and swirl to mix. Allow the sample to stand for 10 minutes.
   3. Filter the solution and proceed with the test using the filtrate in Steps 7 and 9 above. The result will be the mg/l of soluble orthophosphate.

D. The PhosVer III Phosphate Reagent Powder may cause some turbidity depending on a large number of factors. It is highly recommended that a reagent blank of PhosVer III Phosphate Reagent Powder in about 25 ml demineralized water be used to zero the instrument in Step 9.

E. The results may be expressed as mg/l phosphorus (P) by dividing the final scale reading by 3. To obtain the mg/l phosphorus pentoxide (P_2O_5), multiply the final reading by 0.75.

6.5.8.7 Calculations

The concentration of phosphate (total inorganic and organic) is read directly from the instrument. As indicated in Steps 11 and 12 (Section 6.5.8.6), the concentration of inorganic phosphate is measured directly from the instrument, and the concentration of total organic phosphate is determined by subtracting the amount of total inorganic phosphate from the results of the total phosphate concentration.

6.5.8.8 Precision and Accuracy

Thirty-three analysts in nineteen laboratories analyzed natural water samples containing exact increments of organic phosphate, with the following results:

Increment as Total Phosphorus mg P/liter	Precision as Standard Deviation mg P/liter	Accuracy as	
		Bias, %	Bias mg/P liter
0.110	0.033	+ 3.09	+0.003
0.132	0.051	+11.99	+0.016
0.772	0.130	+ 2.96	+0.023
0.882	0.128	- 0.92	-0.008

6.5.9 Sulfite Analysis

6.5.9.1 Scope and Application

This method is applicable to aqueous samples of low turbidity and color or where filtration will not result in loss of sulfite. Silica in excess of 500 mg/l and large amounts of organic matter will interfere with precipitation yielding low results. Nitrite should be absent.

6.5.9.2 Summary of Method

This method makes use of the colloidal precipitate formed by sulfate ($SO_4^=$) and barium chloride under strongly acidic conditions. One sample aliquot is precipitated with $BaCl_2$ reagent and its turbidity is measured. 30% hydrogen peroxide is added to a second aliquot to oxidize the sulfite to sulfate. This second aliquot is then precipitated with $BaCl_2$ reagent. The difference in turbidity can then be related to the sulfite concentration.

6.5.9.3 Definitions

No unique terminology is used in this method.

6.5.9.4 Apparatus

- Portable Test Kit Spectrophotometer for use at 445 nm.
- Standard laboratory glassware.

6.5.9.5 Reagents

- SulfaVer IV powder pillows, Hach No. 12065.
- 30% H_2O_2, J.T. Baker No. 2186

6.5.9.6 Procedure

1) The sample cannot be preserved. It must be analyzed as soon as possible after collection.
2) Add 25.0 ml of sample (less if high in sulfate) to each of two sample cells, A and B. If the sample is turbid, filter through Whatman No. 2 paper. Add 25 ml H_2O to a third sample cell to act as a blank.
3) To cell A, add 0.5 ml of 30% H_2O_2 and mix. Allow this mixture to stand at least three minutes. To cell B add 0.5 ml of H_2O and mix.

4) Add a package of SulfaVer IV to each of the three samples and mix until dissolved. Wait about ten minutes to allow turbidity to develop.

5) Set wavelength dial to 450 ml. Place cell C in sample holder and use light control knob to set meter at zero miligrams per liter. Record readings for cells A and B.

6.5.9.7 Calculations

$$\text{Sulfite concentration} = \frac{80}{96}(A-B)$$

A = Reading for Cell A

B = Reading for Cell B

If sample size is other than 25 ml multiply the above result by

$$\frac{X}{25} \text{ where}$$

X = ml of sample used (should be same for A and B)

6.5.9.8 Accuracy and Precision

This method is accurate to 1 mg/l. A synthetic unknown containing 259 mg/l sulfate was analyzed in 19 laboratories by the turbidimetric method, with a relative standard deviation of 9.1% and a relative error of 1.2%.

6.5.10 Sulfate

6.5.10.1 Scope and Application

Method is applicable to drinking and surface waters, domestic and industrial wastes. The method is suitable for all ranges of sulfate; however, for reliable readings, sample aliquots containing not more than 40 mg/l SO_4 should be used.

6.5.10.2 Summary of Method

Sulfate ion is converted to a barium sulfate suspension under controlled conditions, using Hach SulfaVer IV Sulfate Reagent (barium chloride). The resulting turbidity is determined spectrophotometrically at 450 nm.

6.5.10.3 Interferences

Silica in excess of 500 mg/l will interfere. The test is not temperature dependent.

6.5.10.4 Apparatus

Hach Portable Test Kit spectrophotometer for use at 450 nm. Standard laboratory glassware.

6.5.10.5 Reagents

- Hach SulfaVer IV Sulfate Reagent Powder Pillow.
- Sulfate standard solution, 50 mg/l SO_4.

6.5.10.6 Procedure*

1. Fill a clean sample cell with sample to the 25 mark. See Note A.
2. Add the contents of one SulfaVer IV Sulfate Reagent Powder Pillow and swirl to mix. A white turbidity will form if sulfate is present. Allow at least 5 minutes but not more than 15 minutes for the turbidity to fully develop before completing Steps 2 and 4. See Note B.

---

* Abstracted from Hach Direct Reading Engineers Laboratory Methods Manual (DR-EL/2).

3. Fill another sample cell to the 25 mark with some of the original water sample and place it in the cell holder. Insert the Sulfate (SulfaVer IV Method) Meter Scale in the meter and adjust the Wavelength Dial to 450 nm. Adjust the LIGHT CONTROL for a meter reading of zero mg/l.
4. Place the prepared sample in the cell holder and read the mg/l sulfate (SO_4).

   Notes:

   A. Filtering is recommended for highly colored and/or turbid water samples. Large amounts of color and/or tubidity will interfere and cause high readings. The filtered sample is then used in Steps 1 and 3.

   B. The sample should not be disturbed during the 5-minute turbidity development period. Results will not be affected if the SulfaVer IV Sulfate Reagent Powder does not completely dissolve.

6.5.10.7 Calculation

As indicated above, the concentration of sulfate is read directly from the instrument.

6.5.10.8 Comment

After each test the sample cells should be cleaned using a brush and soap. If this is not done soon after each test, a white film will develop on the inside of the cells and lead to errors in future tests.

6.5.10.9 Precision and Accuracy

Thirty-four analysts in sixteen laboratories analyzed six synthetic water samples containing exact increments of inorganic sulfate with the following results:

Increment as Sulfate mg/liter	Precision as Standard Deviation mg/liter	Accuracy as	
		Bias %	Bias mg/liter
8.6	2.30	-3.72	-0.3
9.2	1.78	-8.26	-0.8
110	7.86	-3.01	-3.3
122	7.50	-3.37	-4.1
188	9.58	+0.04	+0.1
199	11.8	-1.70	-3.4

6.5.11 Cyanide, Free

6.5.11.1 Scope and Application

This method is applicable to the determination of free cyanide in saline and non-saline waters, domestic and industrial wastes. If a total cyanide concentration value is required, i.e., a value for both free and complex cyanides, a distillation must be performed prior to analysis.[1]

6.5.11.2 Summary of Method

Free cyanide is determined colorimetrically using the prepackaged Hach Model CYN-2 Cyanide Test Kit. Although the contents of the "Powder Pillows" used in the reaction are not stated, it is quite probable that as in the standard colorimetric measurement procedure the cyanide is converted to cyanogen chloride, $CNCl$, by reaction with chloramine -T at a pH less than 8. When this reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridine-barbituric acid reagent. The color intensity is then compared with standard colors to determine the free cyanide content of the sample.

6.5.11.3 Interferences

Although the Hach procedure[2] does not discuss interferences, it is most probable that sulfides would adversely affect this procedure, as well as the standard colorimetric technique.

If a drop of sample on lead acetate test paper indicates the presence of sulfides, treat 25 ml more of the stabilized sample ($pH \geq 12$) than that required for the cyanide determination with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate, measure the sample to be used for analysis. Avoid a large excess of cadmium and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material.

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[1] Distillation procedure may be found in ASTM Standards, Part 23, Water: Atmospheric Analyses, p. 498, Method D2036-72 Reference Method A(p 173).

[2] Hach Direct Reading Engineers Laboratory Methods Manual (DR-EL/2).

6.5.11.4 Sample Handling and Preservation

Samples should be analyzed as rapidly as possible after collection. If storage is required, the samples should be stored in a refrigerator or in an ice chest filled with water and ice to maintain temperature at 4°C.

If a sample were to be returned to the laboratory for subsequent distillation and total cyanide analysis, the sample should be collected in plastic bottles of 1 liter or larger size. (All bottles must be throughly cleansed and thoroughly rinsed to remove soluble material from containers.) The sample must also be preserved with 2 ml of 10 N sodium hydroxide per liter of sample ($pH \geq 12$) at the time of collection.

6.5.11.5 Apparatus

- Hach Portable Test Kit Spectrophotometer
- Standard laboratory glassware.

6.5.11.6 Reagents

Reagents for the Hach Model C4N-2 Cyanide Test Kit include the following:

1) Metal Inhibitor Powder Pillow
2) CyaniVer I Powder Pillow
3) CyaniVer II Powder Pillow

6.5.11.7 Procedure

1) If the water sample is turbid, filter a sample for testing. To do this, place the funnel on one of the square mixing bottles. Place a piece of folded filter paper in the funnel. Pour the water sample into the filter paper and allow it to pass through. Filter enough sample to fill the square mixing bottle up to the shoulder.
2) Add the contents of one Metal Inhibitor Powder Pillow to the filtered sample. Swirl to mix.
3) Add the contents of one CyaniVer I Powder Pillow. Swirl to mix and dissolve.
4) Add the contents of one CyaniVer II Powder Pillow. Swirl to mix and dissolve. If cyanide is present, a pink color will develop in a short time. Allow 15 minutes for color development, during which the color becomes progressively more purple,

and will then become a true blue. Swirl the sample bottle from time to time to aid in dissolving the powders. (See Note A).

5) Fill a color viewing tube to the 5 ml mark with the prepared sample, and place it in the right opening in the comparator.
6) Fill the other color viewing tube to the 5 ml mark with clear water and place it in the left opening in the comparator.
7) Rotate the color disc until a color match is obtained. Read the ppm Cyanide (CN) from the scale window.

NOTES:

A. Fifteen minutes is the time usually required at 25°C. If the sample is colder, a longer time will be required, and if warmer, a shorter time. In all cases, wait until the color changes to a true blue, with no trace of red remaining. If the sample stands too long, the color will eventually turn a greenish-blue. If over-development occurs, repeat the test.

6.5.11.8 Calculations

The free cyanide concentration of the sample is read directly from the scale window on the colorimeter in this test kit.

6.5.11.9 Precision and Accuracy

There are no data available at this time on the precision or accuracy of this method.

6.5.12 Ammonia Nitrogen

6.5.12.1 Scope and Application

The method covers the determination of ammonia in drinking, surface and saline waters, domestic and industrial wastes in the range of 0-2 mg/l.

6.5.12.2 Summary of Method

The sample is reacted with Nessler Reagent (a solution of mercuric iodide in the presence of potassium iodide). The yellow color which develops is proportional to the concentration of ammonia present, which is determined spectrophotometrically at 425 nm.

6.5.12.3 Interferences

If the hardness of the water sample is above 100 mg/l (about 6 grains) a precipitate of magnesium hydroxide may form a slight turbidity and cause high readings. One drop of Rochelle Salt Reagent added to each sample will eliminate this interference.

Iron and sulfide will interfere by causing a turbidity with the Nessler Reagent. Less common interferences such as hydrazine, glycine, aliphatic and aromatic amines, organic chloramines, acetone, aldehydes, and alcohols may cause greenish or other off-colors, or turbidity. These interferences can be overcome by distilling the sample before making the test.

6.5.12.4 Apparatus

Hach Portable Test Kit spectrophotometer for use at 425 nm. Standard laboratory glassware.

6.5.12.5 Reagents

- Nessler reagent
- Rochelle salt reagent
- Ammonia Nitrogen Standard Solution, 1.0 mg/l

6.5.12.6 Procedure*

1. Fill a clean 25 ml graduated cylinder with sample to the 25 ml mark. Pour into a clean sample cell.
2. Measure 25 ml of demineralized water by filling another clean 25 ml graduated cylinder to the 25 ml mark. Pour the demineralized water into another clean sample cell. See Note A.
3. Using the 1 ml calibrated dropper, add 1 ml of Nessler Reagent to each sample cell and swirl to mix. See Note B. A yellow color will develop if ammonia nitrogen is present. Allow at least 10 minutes, but not more than 25 minutes for the color

to fully develop before performing Steps 4 and 5.

4. Place the sample cell containing the prepared demineralized water solution in the cell holder. Insert the Nitrogen, Ammonia (Nessler Method) Meter Scale in the meter and adjust the Wavelength Dial to 425 nm. Adjust the LIGHT CONTROL for a meter reading of zero mg/l.
5. Place the prepared sample in the cell holder and read the mg/l ammonia nitrogen (N). See Note C.

Notes:

A. The temperature of the demineralized water and the water sample should be 20° ± 1°C (68° ± 2°F) for best results. Higher temperatures will cause high readings and lower temperatures will cause low results.

B. A slight precipitate in the Nessler Reagent is normal. These solids should not be disturbed when transferring the reagent. If the Nessler Reagent turns a dark brown, it should be discarded and a fresh supply ordered.

C. The results may be expressed as mg/l ammonia (NH_3) or mg/l ammonium (NH_4) by multiplying the final scale reading by 1.22 or by 1.29, respectively.

6.5.12.7 Calculation

As indicated above, the concentration of ammonia is read directly from the spectrophotometer.

6.5.12.8 Precision and Accuracy

Data are unavailable on the precision and accuracy of the method.

---

* Abstracted from Hach Direct Reading Engineers Laboratory Methods Manual (DR-EL/2).

Figure 6-1. Data Sheet - Acidity

SAMPLE LOCATION ____________
SAMPLE MEDIUM ____________
LOG NUMBER ____________

DATE SAMPLE REC'D ____________
DATE SAMPLE ANALYZED ____________
ANALYZED BY ____________
VERIFIED BY ____________

I	STANDARD REAGENTS USED	REFERENCE METHOD	DATE REAGENT STANDARDIZED
1.	____________	____________	____________
2.	____________	____________	____________
3.	____________	____________	____________
4.	____________	____________	____________

II	CALIBRATION CURVE RUN	DATE CALIBRATION RUN
1.		
2.		
3.		
4.		

III CALCULATIONS

Methyl orange acidity mg/l
$CaCO_3 = 100 \times V_1 \times N$
V_1 = volume of titrant
= ____________ml
N = normality of titrant
= ____________
Acidity = ____________ mg/l $CaCO_3$

Phenolphthalein acidity, mg/l
$CaCO_3 = 100 \times V_2 \times N$
V_2 = volume of titrant
= ____________ml
N = normality of titrant
= ____________
Acidity = ____________ mg/l $CaCO_3$

IV SPECIFIC COMMENTS ON SAMPLE CHARACTERISTICS

VISUAL ____________
ODOR ____________
COLOR ____________
SPECIFIC COMMENTS ON SAMPLE ANALYSIS ____________
VISUAL ____________
ODOR ____________
ERROR OBSERVATIONS ____________

Figure 6-2. Data Sheet - Alkalinity

SAMPLE LOCATION ______________ DATE SAMPLE REC'D ______________

SAMPLE MEDIUM ______________ DATE SAMPLE ANALYZED ______________

LOG NUMBER ______________ ANALYZED BY ______________

VERIFIED BY ______________

I STANDARD REAGENTS USED REFERENCE METHOD DATE REAGENT STANDARDIZED

	STANDARD REAGENTS USED	REFERENCE METHOD	DATE REAGENT STANDARDIZED
1.			
2.			
3.			
4.			

II CALCULATIONS

TOTAL ALKALINITY

$$\text{As mg/liter } CaCO_3 = \frac{V_{acid} \times N_{acid} \times 50{,}000}{V_{sample}} = 20^* \text{ Vacid}$$

* Valid when Nacid = 0.02 N, and Vsample = 50 ml

III SPECIFIC COMMENTS ON SAMPLE CHARACTERISTICS

VISUAL ______________

ODOR ______________

COLOR ______________

SPECIFIC COMMENTS ON SAMPLE ANALYSIS ______________

VISUAL ______________

ODOR ______________

ERRORS OBSERVED ______________

Figure 6-3. Data Sheet - Conductivity

SAMPLE LOCATION ______________ DATE SAMPLE REC'D ______________

SAMPLE MEDIUM ______________ DATE SAMPLE ANALYZED ______________

LOG NUMBER ______________ ANALYZED BY ______________

VERIFIED BY ______________

I CALCULATIONS

$$G = \frac{1 \times 10^6 C}{R(1+0.0200 (t-25)}$$

where R = Resistance of Sample
C = Cell Constant
t = temp, °C

= (Meter Reading* x Scale Factor x C)

*Applicable for field meter with temp compensation

II SPECIFIC COMMENTS ON SAMPLE CHARACTERISTICS

VISUAL ______________________________

ODOR ______________________________

COLOR ______________________________

SPECIFIC COMMENTS ON SAMPLE ANALYSIS ______________________________

VISUAL ______________________________

ODOR ______________________________

ERRORS OBSERVED ______________________________

Figure 6-4. Data Sheet - Hardness

SAMPLE LOCATION ____________ DATE SAMPLE REC'D ____________

SAMPLE MEDIUM ____________ DATE SAMPLE ANALYZED ____________

LOG NUMBER ____________ ANALYZED BY ____________

VERIFIED BY ____________

I CALCULATIONS

mg/liter Total Hardness = Number of ml Titrant x 20
(as $CaCO_3$)

II SPECIFIC COMMENTS ON SAMPLE CHARACTERISTICS

VISUAL ____________

ODOR ____________

COLOR ____________

SPECIFIC COMMENTS ON SAMPLE ANALYSIS ____________

VISUAL ____________

ODOR ____________

ERRORS OBSERVED ____________

Figure 6-5. Data Sheet - pH

SAMPLE LOCATION ____________ DATE SAMPLE REC'D ____________

SAMPLE MEDIUM ____________ DATE SAMPLE ANALYZED ____________

LOG NUMBER ____________ ANALYZED BY ____________

VERIFIED BY ____________

I CALIBRATION CURVE RUN ON BUFFER SOLN: DATE CALIBRATION RUN

1. pH 4 BUFFER
2. pH 7 BUFFER
3. pH 10 BUFFER
4.

II CALCULATIONS

pH units = Direct Reading from Meter

III SPECIFIC COMMENTS ON SAMPLE CHARACTERISTICS

VISUAL ____________

ODOR ____________

COLOR ____________

SPECIFIC COMMENTS ON SAMPLE ANALYSIS ____________

VISUAL ____________

ODOR ____________

ERRORS OBSERVED ____________

6.6 OPACITY MEASUREMENTS (MODIFIED EPA METHOD 9)

6.6.1 Scope and Application

The opacity of emissions from stationary sources is determined visually. This method is applicable for the determination of the opacity of emissions from stationary sources. Also see Section 5.2.11.

6.6.2 Procedure

The observer shall use the following procedures for visually determining the opacity of emissions:

Position. The observer shall stand at a distance sufficient to provide a clear view of the emissions with the sun oriented in the 140^{0} sector to his back. Consistent with maintaining the above requirement, the observer shall, as much as possible, make his observations from a position such that his line of vision is approximately perpendicular to the plume direction, and when observing opacity of emissions from rectangular outlets (e.g., roof monitors, open baghouses, noncircular stacks), approximately perpendicular to the longer axis of the outlet. The observer's line of sight should not include more than one plume at a time when multiple stacks are involved, and in any case, the observer should make his observations with his line of sight perpendicular to the longer axis of such a set of multiple stacks (e.g. stub stacks on bag-houses).

Field Records. The observer shall record the name of the plant, emission location, type facility, observer's name and affiliation and the date on a field data sheet (Figure 6-6 and 6-7). The time, estimated distance to the emission location, approximate wind direction, estimated wind speed, description of the sky condition (presence and color of clouds), and the plume background are recorded on a field data sheet at the time opacity readings are initiated and completed.

Observations. Opacity observations shall be made at the point of greatest opacity in that portion of the plume where condensed water vapor is not present. The observer shall not look continuously at the plume, but instead shall observe the plume momentarily at 15-second intervals.

Attached Steam Plumes. When condensed water vapor is present within the plume as it emerges from the emission outlet, opacity observations shall be made beyond the point in the plume at which condensed water vapor is no longer visible. The observer shall record the approximate distance from the emission outlet to the point in the plume at which the observations are made.

RECORD OF VISUAL DETERMINATION OF OPACITY

PAGE____of____

COMPANY____________
LOCATION____________
TEST NUMBER____________
DATE____________
TYPE FACILITY____________
CONTROL DEVICE____________

HOURS OF OBSERVATION____________
OBSERVER____________
OBSERVER CERTIFICATION DATE____________
OBSERVER AFFILIATION____________
POINT OF EMISSIONS____________
HEIGHT OF DISCHARGE POINT____________

CLOCK TIME	Initial			Final
OBSERVED LOCATION Distance to Discharge				
Direction from Discharge				
Height of Observation Point				
BACKGROUND DESCRIPTION				
WEATHER CONDITIONS Wind Direction				
Wind Speed				
Ambient Temperature				
SKY CONDITIONS (clear, overcast, % clouds, etc.)				
PLUME DESCRIPTION Color				
Distance Visible				
OTHER INFORMATION				

SUMMARY OF AVERAGE OPACITY

Set Number	Time	Opacity	
	Start--End	Sum	Average

Readings ranged from____to______% opacity

The source was/was not in compliance with____at the time evaluation was made.

Figure 6-6. Record of Visual Determination of Opacity

OBSERVATION RECORD PAGE__OF__

COMPANY__________
LOCATION__________
TEST NUMBER__________
DATE __________

OBSERVER__________
TYPE FACILITY__________
POINT OF EMISSIONS __________

Hr.	Min.	Seconds				Steam Plume (Check if applicable)		Comments
		0	15	30	45	Attached	Detached	
	0							
	1							
	2							
	3							
	4							
	5							
	6							
	7							
	8							
	9							
	10							
	11							
	12							
	13							
	14							
	15							
	16							
	17							
	18							
	19							
	20							
	21							
	22							
	23							
	24							
	25							
	26							
	27							
	28							
	29							

OBSERVATION RECORD
(Continued) PAGE__OF__

COMPANY__________
LOCATION __________
TEST NUMBER__________
DATE __________

OBSERVER__________
TYPE FACILITY__________
POINT OF EMISSIONS__________

Hr.	Min.	Seconds				Steam Plume (Check if Applicable)		Comments
		0	15	30	45	Attached	Detached	
	30							
	31							
	32							
	33							
	34							
	35							
	36							
	37							
	38							
	39							
	40							
	41							
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	47							
	48							
	49							
	50							
	51							
	52							
	53							
	54							
	55							
	56							
	57							
	58							
	59							

Figure 6-7. Observation Record

Detached Steam Plume. When water vapor in the plume condenses and becomes visible at a distinct distance from the emission outlet, the opacity of emissions should be evaluated at the emission outlet prior to the condensation of water vapor and the formation of the steam plume.

Recording Observations. Opacity observations shall be recorded to the nearest 5 percent at 15-second intervals on an observational record sheet. (See Figure 6-7 for an example.) A minimum of 24 observations shall be recorded. Each momentary observation recorded shall be deemed to represent the average opacity of emissions for a 15-second period.

6.6.3 Calculations

Opacity shall be determined as an average of 24 consecutive observations recorded at 15-second intervals. Divide the observations recorded on the record sheet into sets of 24 consecutive observations. A set is composed of any 24 consecutive observations. Sets need not be consecutive in time and in no case shall two sets overlap. For each set of 24 observations, calculate the average by summing the opacity of the 24 observations and dividing this sum by 24. If an applicable standard specifies an averaging time requiring more than 24 observations, calculate the average for all observations made during the specified time period. Record the average opacity on a record sheet. (See Figures 6-6 and 6-7 for an example).

6.6.4 Accuracy and Precision

The use of a qualified observer has been waived for this program. Therefore previously determined accuracy and precision cannot be relied on. The results should be expected to fall well within the established limits for this program.

6.7 BACHARACH SMOKE SPOT TEST

The Bacharach test is used in the field to supplement the Ringelmann test. The Bacharach test uses a small plunger pump to pull a sample of the duct effluent through an inserted filter, thus causing a gray color spot on the filter. This color spot is then compared to a standard scale and the appropriate density reading is chosen which corresponds to the filter shade. The step-by-step procedure for a Bacharach test is presented below.

6.7.1 Procedure

The following procedure has been abstracted from the instruction manual for the "True-Spot" Model RCC-B Bacharach test kit.

1. Tear a strip from the perforated filter paper sheet (supplied in the test kit "smoke scale" envelope). Loosen the clamp screw in the plunger pump and insert the end of the paper strip into the slot (see Figure 6-8). Tighten the clamp screw and release the sampling tube from the rubber barrel clip.
2. Insert the sampling tube at least 2-1/2 inches into the flue through a 1/4-inch diameter hole located between the furnace/boiler flue outlet and draft regulator.
3. Pull the pump handle through ten full pump strokes (Figure 6-9).
4. Remove the sampling tube from the flue, loosen the clamp screw and remove the filter paper.
5. Match the color of the smoke spot on the filter paper strip to the closest spot on the smoke scale provided. In comparing the color of the smoke spot to the chart, slide the filter paper strip between the back of the smoke scale and the white plastic slide viewing the smoke spot on the filter paper through the window in the center of the color spots on the smoke scale with the smoke spot backed by the white plastic slide (see Figure 6-10).
6. Take additional samples as required by clamping the filter paper strip in the slot so that the previous spot is the visible outside spot.

6.7.2 Comments

The True-Spot Model RCC-B test kit plunger pump should be warmed to room temperature before sampling begins. This will retard moisture build-up in condensate traps.

After every 10th sample, the sampling tube should be tapped to loosen soot and rust. The pump should also be purged with several rapid pump strokes to draw in room air (without filter paper in the slot).

When obtaining a sample, a steady pull motion should be used so that a full stroke is obtained in 3 or 4 seconds.

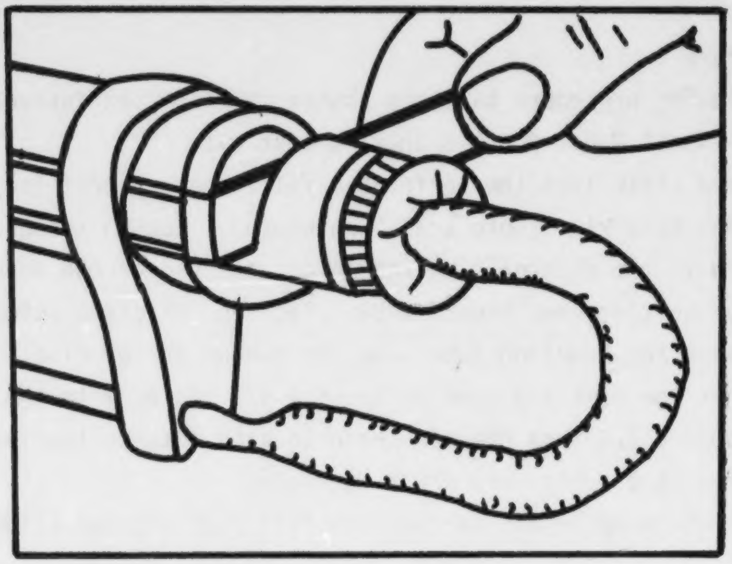

Figure 6-8. Insertion of Filter Paper Strip Into Bacharach Test Plunger Pump

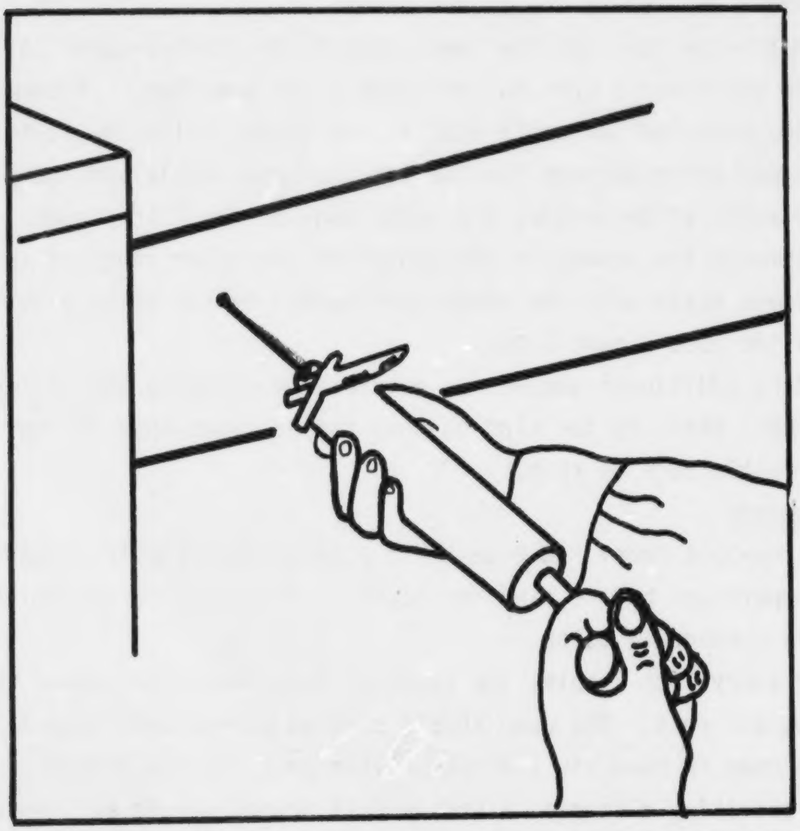

Figure 6-9. Procedure for Obtaining a Sample Using the Bacharach Smoke Spot Test Plunger Pump

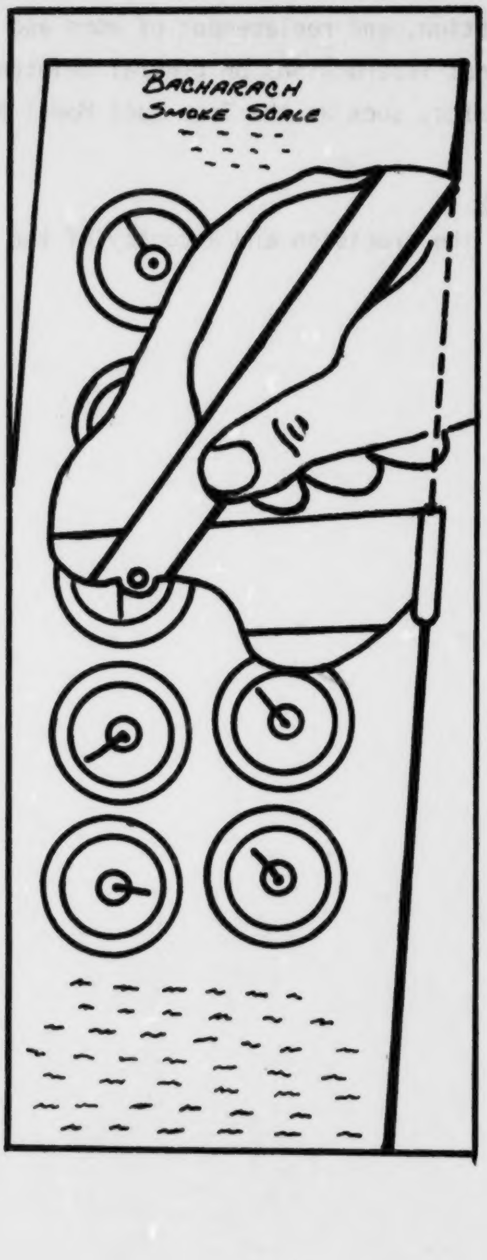
BACHARACH
SMOKE SCALE

Figure 6-10. Procedure for Analysis of Smoke Spot on Bacharach Scale

For maximum accuracy, the smoke scale should be held at arm's length when comparing the smoke spot on the filter paper. The smoke scale should be kept clean and stored in an envelope when not in use.

The test kit apparatus should be subjected to periodic inspection and maintenance. This includes emptying condensate traps, checking for leakage, periodic cleaning and lubrication, and replacement of worn and damaged parts as required. (Additional instructions on general maintenance and operation of Bacharach test kits, such as the True Spot Model RCC-B, are provided with each kit).

6.7.3 Precision and Accuracy

Data are unavailable on the precision and accuracy of the Bacharach test.

7.0 ORGANIC ANALYSIS PROCEDURES

7.1 INTRODUCTION

The analytical procedures presented in this chapter are designed for use in Level 1 surveys where it is important both to evaluate the overall emissions from a large number of sources in a cost effective manner and to ascertain that relevant information about actual or potential emissions problems is properly obtained and utilized. The objective of the procedures given here is to provide an estimate of the predominant classes of organic compounds present in a given sample. Thus, the procedures comprising this total methodology are intended to determine the presence or absence of all major classes of organic compounds within the prescribed level of accuracy for a Level 1 analysis.

In addition to the information generated by the Level 1 procedures, the EPA has additional specific needs for data on the nature and quantity of all polynuclear aromatic hydrocarbons (PAH) present in samples and any unique materials identified in specific LC fractions. For this reason, "Level 2" analytical gas chromatography/mass spectrometry (GC/MS) procedures for these materials are provided in the Level 1 analysis scheme.

The samples obtained in accordance with the procedures outlined in Chapter 5 will be liquids or solids. Chapter 3 discusses procedures for the apportionment of samples between inorganic and organic analyses.

7.2 LEVEL 1 ORGANIC ANALYSIS METHODOLOGY

An overview of the sources of the samples and the appropriate combinations of the samples for analysis is shown in Figure 7-1. The exact handling procedures for disbursing these samples is described in Chapter 4.0 and Figures 4-3 and 4-4. The overview of the methodology used for the Level 1 organic analysis is shown in Figure 7-2 and includes sample preparation for analysis, decision criteria, and the appropriate section for each procedure. It is assumed that the initial samples have already been combined and apportioned for the organic and inorganic analyses (see Chapter 4). The XAD-2 module samples will have to be combined for analysis after preliminary workup.

As of 1 August, 1978, a directed program change requires that all SASS train organic rinses and extracts from gas and oil (distillate and residual) fired sites be combined into a single sample (Section 7.3.3). Treatment of condensate extract samples from these sites is not affected; they are treated in the usual manner.

As indicated in Figures 7-1 and 7-2, the extent of sample preparation required varies with sample type. The low molecular weight hydrocarbons (boiling at $\leq 90^{\circ}C$) are determined by gas chromatography on-site as described in Section 6.2 and require negligible preparation. Organic liquids will not need pretreatment. The majority of the samples, however, such as SASS train components, aqueous solutions, bottom ashes, and other solids require an initial solvent extraction (Section 7.3) to separate the organic and inorganic portions of the samples before the analyses can proceed.

Both the extracts and the neat organic liquids are then concentrated in a Kuderna-Danish evaporator to a 10 ml volume (Section 7.4). Two 1 ml aliquots are then taken from each concentrate for the following analyses: 1) total chromatographable organic material (GC-TCO, Section 7.7) and GC/MS analysis, should Level 2 efforts be required (Section 7.10); and 2) gravimetric determination of non-volatile organic material (Section 7.5) and an infrared analysis on the residue from the gravimetric determination (Section 7.6)

The data provided by performing the TCO and the gravimetric analyses are now used to make the decision as to the analysis path to be followed for all other determinations. The TCO analysis provides quantitative information on the bulk amount of semi-volatile organic material in the boiling range of the C7 to C16 alkanes--90° to $300^{\circ}C$. The gravimetric analysis provides quantitative results on the amount of nonvolatile organics in the sample. These two values combine to give an estimate of the total organic content of the sample. If the total organic content of the sample is equivalent to a stack concentration of 500 $\mu g/m^3$ or less, the organic analysis is terminated. If the value is greater than 500 $\mu g/m^3$ stack concentration, the direction of the analyses will depend on the TCO, which is the volatile content of the sample.

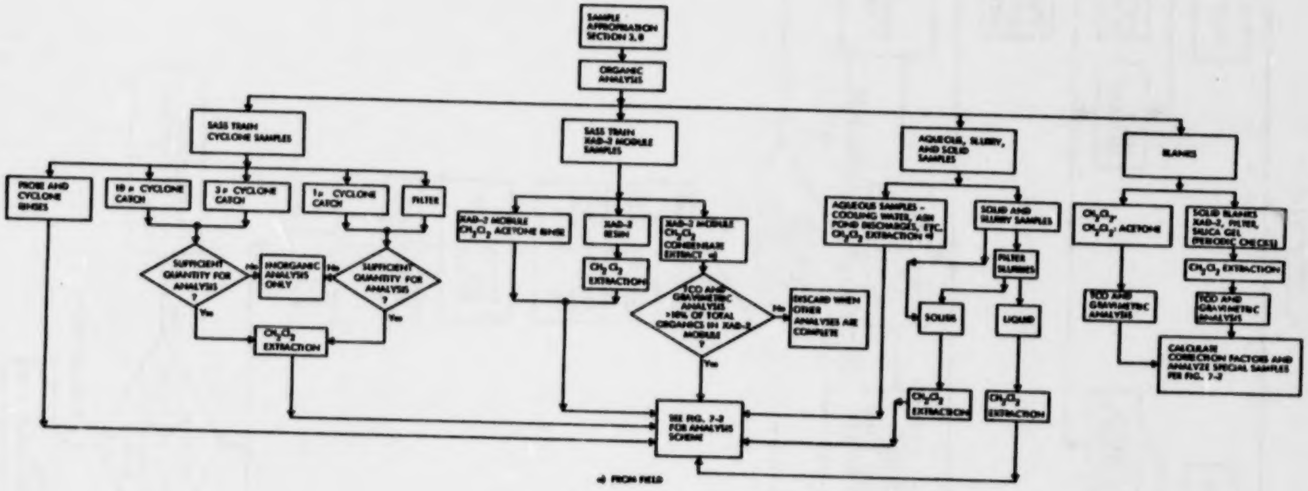
SAMPLE APPROPRIATION SECTION 3.0
ORGANIC ANALYSIS
SASS TRAIN CYCLONE SAMPLES
SASS TRAIN XAD-2 MODULE SAMPLES
AQUEOUS, SLURRY, AND SOLID SAMPLES
BLANKS
PROBE AND CYCLONE RINSES
10 μ CYCLONE CATCH
3 μ CYCLONE CATCH
1 μ CYCLONE CATCH
FILTER
SUFFICIENT QUANTITY FOR ANALYSIS ?
No
INORGANIC ANALYSIS ONLY
No
SUFFICIENT QUANTITY FOR ANALYSIS ?
Yes
Yes
CH_2Cl_2 EXTRACTION
XAD-2 MODULE CH_2Cl_2 ACETONE RINSE
XAD-2 RESIN
CH_2Cl_2 EXTRACTION
XAD-2 MODULE CH_2Cl_2 CONDENSATE EXTRACT ◄)
TCO AND GRAVIMETRIC ANALYSIS >10% OF TOTAL ORGANICS IN XAD-2 MODULE ?
No
DISCARD WHEN OTHER ANALYSES ARE COMPLETE
Yes
SEE FIG. 7-2 FOR ANALYSIS SCHEME
◄) FROM FIELD
AQUEOUS SAMPLES - COOLING WATER, ASH POND DISCHARGES, ETC. CH_2Cl_2 EXTRACTION ◄)
SOLID AND SLURRY SAMPLES
FILTER SLURRIES
SOLIDS
LIQUID
CH_2Cl_2 EXTRACTION
CH_2Cl_2 EXTRACTION
CH_2Cl_2, CH_2Cl_2/ ACETONE
TCO AND GRAVIMETRIC ANALYSIS
SOLID BLANKS XAD-2, FILTER, SILICA GEL (PERIODIC CHECKS)
CH_2Cl_2 EXTRACTION
TCO AND GRAVIMETRIC ANALYSIS
CALCULATE CORRECTION FACTORS AND ANALYZE SPECIAL SAMPLES PER FIG. 7-2

Figure 7-1. Level 1 Organic Analysis Flow Chart

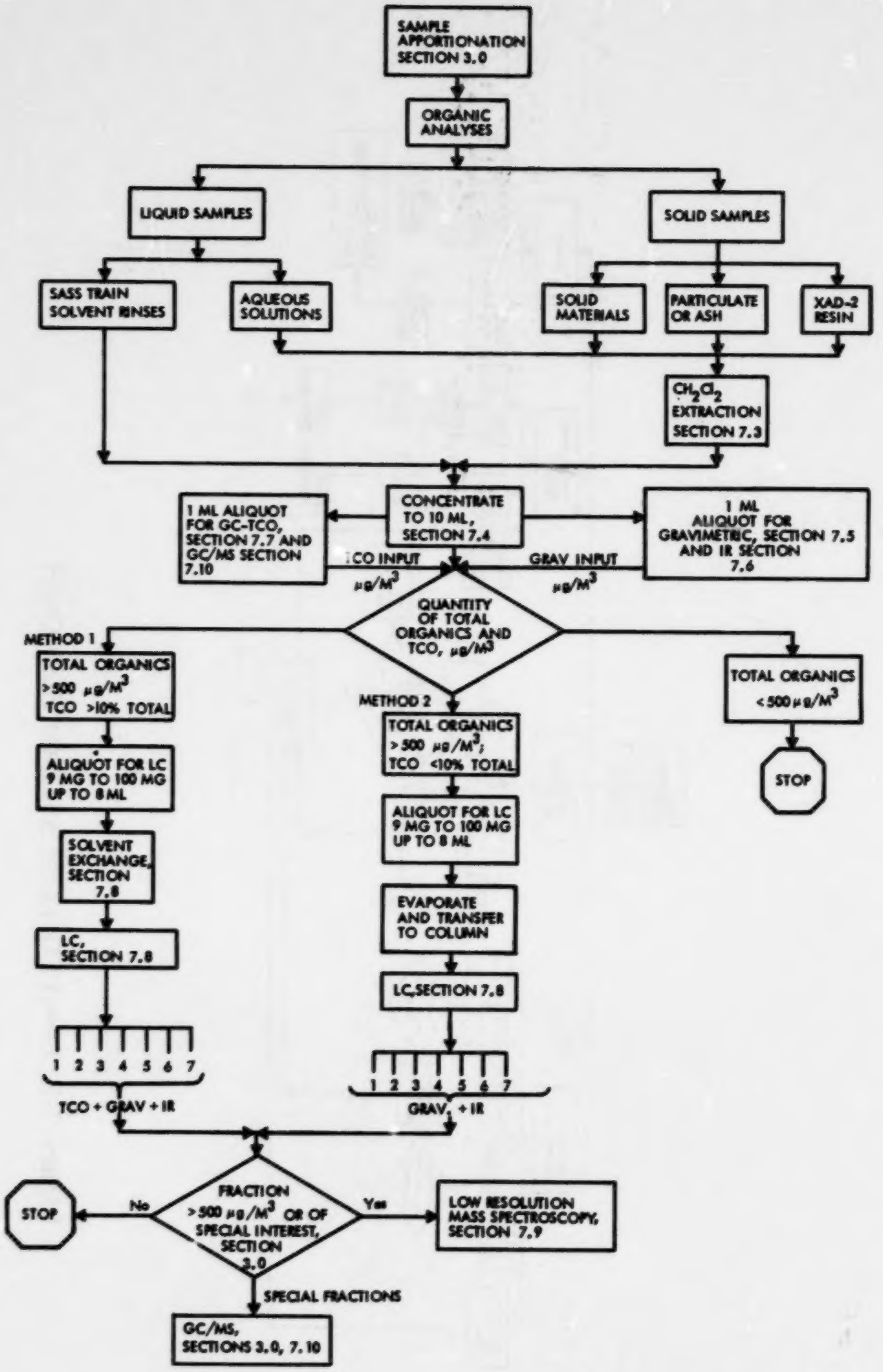
SAMPLE APPORTIONATION SECTION 3.0
ORGANIC ANALYSES
LIQUID SAMPLES
SOLID SAMPLES
SASS TRAIN SOLVENT RINSES
AQUEOUS SOLUTIONS
SOLID MATERIALS
PARTICULATE OR ASH
XAD-2 RESIN
CH2Cl2 EXTRACTION SECTION 7.3
1 ML ALIQUOT FOR GC-TCO, SECTION 7.7 AND GC/MS SECTION 7.10
CONCENTRATE TO 10 ML, SECTION 7.4
1 ML ALIQUOT FOR GRAVIMETRIC, SECTION 7.5 AND IR SECTION 7.6
TCO INPUT µg/M3
GRAV INPUT µg/M3
QUANTITY OF TOTAL ORGANICS AND TCO, µg/M3
METHOD 1
TOTAL ORGANICS >500 µg/M3 TCO >10% TOTAL
METHOD 2
TOTAL ORGANICS >500 µg/M3; TCO <10% TOTAL
TOTAL ORGANICS <500 µg/M3
STOP
ALIQUOT FOR LC 9 MG TO 100 MG UP TO 8 ML
SOLVENT EXCHANGE, SECTION 7.8
ALIQUOT FOR LC 9 MG TO 100 MG UP TO 8 ML
EVAPORATE AND TRANSFER TO COLUMN
LC, SECTION 7.8
LC, SECTION 7.8
1 2 3 4 5 6 7
1 2 3 4 5 6 7
TCO + GRAV + IR
GRAV. + IR
STOP
No
FRACTION >500 µg/M3 OR OF SPECIAL INTEREST, SECTION 3.0
Yes
LOW RESOLUTION MASS SPECTROSCOPY, SECTION 7.9
SPECIAL FRACTIONS
GC/MS, SECTIONS 3.0, 7.10

Figure 7-2. Level 1 Organic Analysis Methodology

If the TCO is less than 10% of the total organic material, the analytical pathway labeled "Method 2" in Figure 7.2 is followed. A suitably sized sample aliquot is taken for liquid chromatographic fractionation, evaporated to dryness and transferred to the LC column (Section 7.8). Each separated fraction is subsequently subjected to gravimetric and infrared analyses (Section 7.5 and 7.6, respectively). Whenever the TCO is greater than 10% of the total organics, an aliquot for LC is prepared by solvent exchange (Section 7.8) to preserve the volatile species. In this "Method 1" procedure, each fraction separated still undergoes gravimetric and infrared analyses; however, the LC fractions are also analyzed for TCO (Section 7.7).

The GC-TCO analysis is used to obtain information on the quantity of material boiling within discrete ranges which are defined by the n-alkanes, C7 through C16, in addition to data on the total amount of material in the n-alkane boiling range. It should be noted that all compounds containing oxygen, nitrogen, sulfur or halogens will also be reported as alkanes. Materials are classified solely on the basis of their retention time relative to the n-alkane, and are quantitated as n-decane.

The infrared analyses provides information on the major functional groups, (i.e., chemical compound classes) present in a sample. Data obtained by the GC-TCO and IR analyses are complementary: many compounds detected in the GC analysis are too volatile to remain for IR analysis, and many compounds detected in the IR analysis have too low a volatility to be detected by the GC-TCO procedure. In a similar manner, the results of GC analyses of the LC fractions complement the IR analyses of these samples.

The remaining sections of this chapter contain procedures for sample handling, preparation, and analysis using the above-mentioned techniques. All classes of compounds and specific individual species identified in the total sample must be accounted for in succeeding determinations.

7.3 EXTRACTION OF SAMPLES FOR ORGANICS

7.3.1 Extraction of Aqueous Samples for Organics

7.3.1.1 Scope and Application

The purpose of this procedure is to prepare liquid samples in the field for subsequent Level 1 and Level 2 analyses for organics. Typical liquid samples that may be generated in this program are aqueous condensates, settling pond samples, and ambient water samples. These liquid extractions are performed with standard separatory funnels. Various sizes of separatory funnels are used depending upon the size of the sample and the estimated level of organics in the sample. Thus, before this procedure is initiated, a decision must be made concerning the appropriate size separatory funnel which must be used.

7.3.1.2 Summary of Method

The sample volume is measured and the sample is transferred to the separatory funnel. If necessary, the pH of the sample is adjusted to neutral with either a saturated solution of sodium bicarbonate or ammonium chloride. The sample is extracted three times with a volume of high-purity methylene chloride that is approximately 5 percent of the sample volume. The resulting extract is measured, dried, and then concentrated, as described in Section 7.4, in preparation for analysis.

7.3.1.3 Definitions

- Sep. funnel - separatory funnel
- MC - methylene chloride

7.3.1.4 Sample Handling

All apparatus (i.e., sample containers, pipets, graduated cylinders, etc.) that contact either the liquid samples or the solvent extracts are to be glass, Teflon, or stainless steel. No grease or lubricant of any kind is to be used on the ground glass joints of the extraction apparatus. All glassware is to be rinsed with high-purity MC.

7.3.1.5 Apparatus

- pHydrion paper in a range of pH 1 to pH 11.
- Separatory funnels with Teflon stopcocks in a range of sizes from 250 ml to 2000 ml.
- Filter tubes, 150 x 24 mm, Corning 9480 or equivalent.

7.3.1.6 Reagents

- Methylene chloride, high purity - suppliers of high purity material are:
  1) Burdick and Jackson, Distilled-in-Glass.®
  2) E. Merck, LiChrosolv.®
  3) Fisher Scientific, HPLC.®
- Acetone, only B&J Distilled-in-Glass is acceptable.
- Ammonium chloride - J. T. Baker, "Baker Analyzed" reagent grade.
- Sodium bicarbonate - J. T. Baker, "Baker Analyzed" reagent grade.
- Anhydrous sodium sulfate, granular, reagent grade - eliminate any organics by heating for 3 hours at 450°C.

7.3.1.7 Procedure

a) Select a separatory funnel approximately twice the volume of the sample to be extracted.

b) Measure the volume of the sample with a graduated cylinder and transfer it to the separatory funnel. Record this volume. Label the funnel with the appropriate sample code identification.

c) Measure the pH of the sample with pH sensitive paper and adjust the pH, if necessary, to neutral. If the pH is less than 6, adjust with $NaHCO_3$ solution. If the pH is greater than 8, adjust with NH_4Cl solution.

d) Pour a volume of MC that is approximately 5 percent of the sample volume (e.g., for a 1000 ml sample, 50 ml of CH_2Cl_2) into the graduated cylinder used to measure the sample volume. Rotate the cylinder to rinse the sides and then transfer the solvent to the separatory funnel.

e) Extract by shaking vigorously for 2 minutes. Allow the layers to separate and draw off the MC layer. Repeat two times and combine the extracts. If an emulsion forms, take appropriate steps (stir, let stand, etc.) to break it before separating the layers.

f) Dry the MC extracts by adding anhydrous Na_2SO_4 and filtering through a glass wool plug.(which has previously been extracted with MC).

g) Measure the volume of the extract with a graduated cylinder.

h) Transfer the total amount of organic extract to an appropriately sized Kuderna-Danish evaporating apparatus and proceed with concentration to 10 ml volume according to Section 7.4.

i) After any change in reagents and with changes in sample type (i.e., requiring pH adjustment), prepare a blank by extracting 1000 ml of deionized water using steps a) through h).

7.3.2 Extraction of Solid Samples for Organics

7.3.2.1 Scope and Application

The purpose of this procedure is to prepare solid samples for subsequent organic analyses. Typical solid samples that may be generated in this program are cyclone catches, particulate filters, XAD-2 resin samples, coal, bottom ashes, and electrostatic precipitator dusts. Various sizes of Soxhlet extractors will be used for this procedure depending upon the size of the sample and the estimated concentration of organics in the sample. Thus, before this procedure is begun, the appropriate size of Soxhlet extractor to be used must be selected.

7.3.2.2 Summary of Method

The sample is placed or weighed into glass thimbles and extracted for 24 hours with high purity methylene chloride. The resulting extracts are concentrated according to the procedure described in Section 7.4, to a final volume of 10 ml.

7.3.2.3 Definitions

MC - Methylene chloride

7.3.2.4 Sample Handling

All equipment (i.e., sample containers, spatulas, tweezers, etc.) that contacts either the solid samples or the solvent extracts is to be glass, Teflon, or stainless steel. No grease or lubricant of any kind is to be used on the ground glass joints of the extraction apparatus.

All glassware is to be rinsed with the same high purity MC used for the sample extraction.

7.3.2.5 Apparatus

- Soxhlet extractors in a range of sizes (Ace Glass sizes A to G) with glass thimbles and condensers.
- Boiling flasks in a range of sizes from 125 ml to 3000 ml with stoppers.
- Heating mantles to fit boiling flasks and variable transformers or steam baths.
- Filter paper, Whatman No. 40.

7.3.2.6 Reagents

- Methylene chloride, Distilled-in-Glass® or equivalent.

7.3.2.7 Procedure

a) Place the sample to be extracted in the glass thimble.

  - XAD-2 resin; weight directly into thimble if the resin is dry. If the resin is wet, follow the procedure in Section 7.3.2.8.
  - Particulate filters; place pre-weighed filter (or portions of filter) in thimble.
  - Ashes, dusts, etc.; weight onto pre-extracted Whatman filter discs, fold into cone shape and place in thimble.

b) Fill the boiling flask 1/2 full with MC.

c) Fit the extractor onto the flask and insert the thimble into extractor and add more solvent to fill the extractor. Label the extractor with the sample code identification. Complete assembly by attaching condenser and clamping entire apparatus in position in heating mantle.

d) Heat the flask sufficiently to produce one discharge cycle about every ten to fifteen minutes. Extract each sample for 24 hours. During the first cycle, check the seating of the ground glass joints by rotating the joints while pushing the condenser/extractor and extractor/flask together. Check for solvent loss periodically throughout the extraction and add solvent as necessary. Record the volume of solvent added.

e) At the completion of the extraction, allow the extractor to cool. Remove the condenser. Pull out the thimble allowing any remaining solvent to drain into the extractor. Transfer the extracted sample to a glass bottle, label with the sample code identification, and return to the sample bank.

f) Siphon off any solvent in the extractor into the boiling flask. Remove the extractor. Measure the volume of the solution with a graduated cylinder. If the Kuderna-Danish concentration cannot be performed immediately, stopper the boiling flask until ready. If the evaporation is to be performed immediately, transfer the extract and rinsings to K-D evaporation apparatus and proceed according to Section 7.4.

g) With every set of samples extracted, prepare a blank by following steps b) through g). Leave the glass thimble empty. If Whatman No. 41 filters are used in the extraction of a set of samples, then the blank is prepared by adding a pre-extracted Whatman No. 41 to the glass thimble.

7.3.2.8 Special Procedure for Preparing XAD-2 Resin for Extraction

XAD-2 resin blanks returned from the field may still be packed in water. All water must be separated from the resin before the Soxhlet extraction with methylene chloride can be performed because the immiscibility of these two solvents hinders extractor operation.

a) Set a tared size F glass Soxhlet thimble in a large glass beaker (greater than 500 ml).

b) Drain as much water from the resin as possible, discarding the water

c) Transfer the resin slurry into the thimble and allow water to drain into the beaker. Discard the water.

d) Wash the resin with 50 ml Distilled-in-Glass acetone. Add the acetone slowly, so it can mix with the water in the resin. The resin will visibly compact as the acetone passes through the thimble. If the resin still seems to contain water, more acetone may be passed through the thimble. Record the total acetone volume used.

e) Retain the acetone for K-D concentration and combination with the methylene chloride extract of the resin as described in Section 7.4.7.

f) Proceed with the extraction of the resin.

g) After completing the extraction, reweigh the thimble and the dry resin to determine the quantity of resin extracted.

7.3.3 Combination of SASS Train Samples

A directed program change (1 August 1978) requires that all SASS train organic rinses and extracts from gas and oil (distillate and residual) fired sites be combined into a single sample. Treatment of condensate from these sites is not affected by this change. This Section describes how these samples are to be combined.

The SASS train samples will be combined on the basis of equal volume percent. The amount of XAD-2 resin taken for organic extraction will determine the percentage of other rinses and extracts to take for combining. Typically, when the XAD-2 sample weighs 150 g, 10 g is taken as a reserve, and 140 g is extracted for organics. Thus, 93.3% of the resin is extracted. Therefore, 93.3% of all other SASS train rinses and extracts are combined with the resin sample extract. The exact percentage is determined by actual weights of resin. Blanks are handled in the same way.

XAD-2 resin samples and blanks, and other SASS train solids, are extracted by Procedure 7.3.2. The combined sample is concentrated by Procedure 7.4. Because the combined sample contains acetone (from probe and module rinses and resin blanks), be sure to use Procedure 7.4.7.f.

7.4 CONCENTRATION OF ORGANIC EXTRACTS

7.4.1 Scope and Application

The purpose of this procedure is to concentrate samples for organic analysis. These samples will be in the form of solvent extracts of solid and liquid samples and of solvent rinses of sampling hardware. The concentrations will be performed with Kuderna-Danish evaporators. Various sizes of evaporators may be used depending upon the size of the sample to be concentrated.

7.4.2 Summary of Method

The solvent extract or rinse sample is transferred to a Kuderna-Danish evaporator. The evaporator apparatus is heated on a steam bath to drive off the solvent. When the sample is sufficiently concentrated, the evaporator is removed from the steam bath and allowed to cool. The sample is then transferred to a 10 ml volumetric flask.

7.4.3 Definitions

K-D - Kuderna-Danish evaporator

MC - Methylene chloride

7.4.4 Sample Handling

All apparatus (i.e., sample containers, flasks, etc.) that contact either the solvent extracts and rinses or the concentrates are to be glass, Teflon, aluminum, or stainless steel. No grease or lubricant of any kind is to be used on the ground glass joints of the concentration apparatus.

All glassware is to be rinsed with high-purity methylene chloride.

7.4.5 Apparatus

a) Steam bath.

b) Kuderna-Danish concentrators consisting of flask (125, 250, and 500 ml), Snyder columns, steel springs, concentrator tubes (10 ml) and adapters as needed.

c) Disposable Pasteur pipets.

d) Class A pipets, 1 mt.

e) Liquid scintillation vials, aluminum-lined caps.

7.4.6 Reagents

a) Methylene chloride, Distilled-in-Glass or equivalent grade

b) Pentane, Distilled-in-Glass

7.4.7 Procedure

a) Select an appropriate size K-D flask and attach a concentrator tube with the steel springs. Place one 3 mm glass bead in the bottom of the tube. Label the K-D flask with the sample code identification.

b) The sample must be dried before it is concentrated. Add 5g of high purity anhydrous Na_2SO_4, which has previously been treated for three hours at 450°C. Shake thoroughly and observe any changes in the solution. If necessary, add more Na_2SO_4 and repeat until the sample appears dry. Filter the solution through a Whatman 41 filter containing glass wool, both of which have previously been extracted with methylene chloride.

c) Transfer the sample to the K-D flask. Rinse the sample container with three 10 ml portions of the same high purity solvent used when the sample was taken. Add the rinsings to the K-D flask.

d) Attach a Snyder column to the K-D flask and clamp the flask in position over the steam bath. The solvent should boil at such a rate that the top ball of the Snyder column bounces lightly.

e) Concentrate the sample to $\sim$5 ml. Should there be sufficient water in the system to form a two-phase system at any time during the evaporation, stop the concentration and remove the water. To avoid losing any organics which might be dissolved in the water, extract it three times with methylene chloride (Section 7.3.1). Combine all the organic extracts and the partially completed organic concentrate in the K-D apparatus as before and resume the evaporation.

f) This step applies only to those samples in which the solvent is an acetone-MC mixture, i.e., probe and module rinses and resin blank extracts. Concentrate these samples to 10 ml. Add 60 ml high purity pentane to ensure the formation of a pentane-acetone (80:20) azeotrope. Reconcentrate to 10 ml. This step occurs very rapidly because the azeotrope boils at 32°C. If instructions have been given to add the XAD-2 extract to the module rinse and/or the probe rinse, this is the time to combine them in the K-D apparatus. Reconcentrate once again to 10 ml.

g) Remove the K-D assembly from the bath and allow to cool. With a disposable pipet, add $\sim$1 ml of methylene chloride to the top of the Snyder column. Allow to drain into K-D flask and then remove the column.

h) Rinse the sides of the K-D flask with another 1-2 ml of solvent. Remove the flask, stopper the concentrator tube and mix the tube contents by shaking vigorously.

i) Transfer the contents of the concentrator tube to a 10 ml volumetric flask. Rinse the tube and stopper with 1-2 ml more of solvent; add these rinsings to the flask and make the flask to standard volume. Label the flask with the sample code identification.

j) With a 1 ml Class A pipet, transfer 1 ml of the concentrate to an ampoule or liquid scintillation vial for TCO analysis and possible subsequent GC/MS analysis. Label the container with the sample code identification.

k) With the same pipet as in step h, transfer a 1 ml aliquot to a liquid scintillation vial for gravimetric and IR analysis. Label the container with the appropriate sample code identification.

7.5 GRAVIMETRIC DETERMINATIONS FOR ORGANICS

7.5.1 Scope and Application

The purpose of this procedure is to determine the weight of nonvolatile organic species in samples for Level 1 organic analyses. The procedure is performed on the concentrates obtained from the Kuderna-Danish concentrations of solvent extract and rinse samples. Weights of organic residues as small as 0.1 mg can be measured.

7.5.2 Summary of Method

The samples are transferred to either small glass beakers (for LC fractions) or tared aluminum weighing dishes. The samples are then evaporated at ambient temperature to a constant weight. The dry samples are always stored in a desiccator.

7.5.3 Sample Handling

All apparatus that contact either the concentrate or evaporated residue samples are to be glass, Teflon, aluminum, or stainless steel. Evaporation of the samples is to be carried out in an area clean of airborne dust and organic vapors that could contaminate the samples.

7.5.4 Apparatus

- Analytical balance capable of weighing 0.1 mg with an accuracy of ±0.03 mg.
- Stainless steel desiccating cabinet with gasket-sealed closure.
- Volumetric pipet, 1 ml, class A.
- Aluminum weighing dishes.
- Glass beakers, 10 to 50 ml.

7.5.5 Reagents

- Methylene chloride, Distilled-in-Glass® or LiChrosolv®
- Pentane, Distilled-in-Glass®
- Methanol, Distilled-in-Glass® or LiChrosolv®

7.5.6 Procedure

a) Rinse the weighing dishes, or beakers with the high purity methylene chloride. Oven dry them at 110°C, then cool in a desiccator. Label with the appropriate sample code identification, weigh to the nearest 0.1 mg, and record the tare weights.

b) For organic concentrate samples, transfer 1 ml of the material from the volumetric flask to the labeled weighing dish with a 1 ml pipet, which has been rinsed with methylene chloride and dried with nitrogen.

c) For LC column fractions, transfer the contents of each volumetric flask to a pre-cleaned, tared, and labeled beaker. Rinse each flask with a small amount of the appropriate solvent and add the rinsings to the beaker.

Rinsing solvents are as follows:
Fraction 1 - Pentane
Fractions 2-4 - Methylene Chloride
Fractions 5-8 - Methanol

d) Allow the samples in the weighing dishes to evaporate at ambient conditions in a clean fume hood until visually dry. Store overnight in the desiccator and then weigh on an analytical balance. Record this weight to the nearest 0.1 mg. If a concentrate is found to weigh less than 10 mg, reweigh the pan plus the sample on a micro-balance. Record this weight to the nearest 0.001 mg.

e) If it was necessary to weigh the sample on a micro-balance, a more accurate tare weight of the pan will be needed. After constant weight has been reached and recorded, rinse the contents from the pan with three successive portions of methylene chloride into another container and allow the pan to air dry in a clean fume hood until visually dry. Store overnight in the desiccator and reweigh the pan on the microbalance. Record this weight to the nearest 0.001 mg. Calculate the sample weight to 3 significant figures.

7.5.7 Calculations

Subtract the tare weight from the final sample weight for each sample. This gives the weight of the organic residue. Multiply the residue weight by the aliquot factor to obtain the total organic residue in the concentrate sample.

$$\begin{matrix}\text{(Final weight-} \\ \text{tare weight)}\end{matrix} \times \frac{\text{Total concentrate volume,}}{\text{Aliquot volume}} = \begin{matrix}\text{Total organic} \\ \text{residue (mg)}\end{matrix}$$

7.6 INFRARED ANALYSIS

7.6.1 Scope and Application

This procedure is used to determine the functional groups present in an organic sample or LC fraction of a partitioned sample. The IR spectra, when interpreted, provide information on functionality (e.g., carbonyl, aromatic hydrocarbon, alcohol, amine, aliphatic hydrocarbon, halogenated organic, etc.). Compound identification is possible only whan a compound is known to be present as a dominant constituent in the sample, which foreknowledge is not likely.

Sample amounts required for this analysis are in the milligram (mg) range with a lower limit of approximately 0.5 mg. A compound must be present in the sample at about 5%-10% (w/w) or more in order for the stronger functional groups of the compound to become apparent for interpretive purposes. Organic solvents, water and some inorganic materials cause interferences. Water and other substances may also cause a decrease in the quality (e.g., resolution of a spectrum, sensitivity) of the analysis.

7.6.2 Summary of Method

The initial organic sample or LC fraction, after evaporation, is either (1) taken up in a small amount of carbon tetrachloride or methylene chloride and transferred to a NaCl window, or (2) mixed with powdered KBr, ground to a fine consistency, and then pressed into a pellet. Whenever LRMS will also be run on the sample, because the criterion weight has been met, the residue is mixed and only a portion taken for the IR scan. A grating IR spectrophotometer is used to scan the sample in the IR region from 2.5 to 15 microns. The spectrum is then interpreted to determine functional group types in the sample.

7.6.3 Definitions

Sample cell - Two NaCl plates with the sample sandwiched in between.

7.6.4 Sample Handling and Preservation

These samples will have been prepared in aluminum weighing dishes or in glass beakers (LC fractions) (Sections 7.5 or 7.8) from which solvent, water and other volatile matter have been removed by evaporation and subsequent desiccation. The samples, when not being used, should be covered and stored in a desiccator containing a drying agent such as silica gel, drierite or an ascarite/silica gel mixture. Samples being stored should also be protected from light in order to avoid deterioration of light sensitive materials.

All glassware and implements must be carefully cleaned, solvent rinsed and dried before use in the analysis of any sample by this procedure. Contact of the sample with hands, unprepared surfaces or any other possible source of contamination must be avoided.

Low resolution mass spectrometry (LRMS) will be performed on the LC fractions which exceed specific quantity criteria (Section 3.0)*. The samples for these analyses will be from the same material on which IR spectra are determined. Therefore, the analyst performing the IR must take care to provide the analyst to be performing the LRMS with a sufficient quantity of homogeneous, uncontaminated sample.

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*LRMS are obtained if a sample residue, when referenced to the source, contains more than the following amounts of material:

Gases	- SASS train samples 0.5 mg/m^3	Solids	1 mg/kg
	- Ambient air-particulates 1$\mu g/m^3$	Aqueous Solutions	0.1 mg/l
	- Ambient air-sorbent trap 0.5 mg/m^3		

A sample aliquot for LRMS will be taken, when required, in the following manner.

a) Dissolve the dried sample in 1 ml spectrograde carbon tetrachloride or methylene chloride. Mix well to ensure homogeneity.

b) Pipet 0.5 ml of the well mixed solution to a clean, labeled, tight sealing container.

c) Refrigerate the LRMS sample.

d) Proceed with the IR analysis on the remaining sample portion.

7.6.5 Apparatus

- Infrared (IR) spectrophotometer, grating dispersion. Perkin-Elmer 283 or equivalent.
- NaCl windows - Configured to fit sample holder of spectrophotometer. Transparent to the IR in the 2.5 to 15 micron region.
- KBr pellet press - Hydraulic type is preferred (Carver Model C or equivalent) but hand-held devices are acceptable, e.g., Perkin-Elmer 186-0436 or equivalent.
- KBr pellet die - To prepare 13 mm diameter or equivalent pellet to contain approximately 1 mg of sample. Perkin-Elmer 186-00250 or equivalent.
- Pipet, Pasteur, disposable - Sargent S-69647-30 or equivalent.
- Standard polystyrene film sample - Normally supplied by instrument manufacturer.

7.6.6 Reagents

- Methylene chloride - Distilled-in-Glass and/or
- Carbon tetrachloride - Distilled-in-Glass
- KBr powder - Spectrograde, dried at 105°C

7.6.7 Procedure

It is possible that two sample forms will occur: (1) an amorphous mass (expected to be the typical sample), and (2) a crystalline or powdery mass. Separate procedures are desirable for these two forms in order to obtain the best available spectra.

7.6.7.1 Procedure for Amorphous Material

Add a few drops of carbon tetrachloride or methylene chloride to solubilize the sample slightly and mix with the tip of a disposable Pasteur pipet. Then using the pipet, take a few drops of this material and transfer to a clean NaCl window. Allow the solvent to evaporate at ambient temperature and then press the two NaCl windows together to spread the sample throughout the area where the IR beam impinges on the plate. Mount the sample cell in the sample compartment of the spectrophotmeter previously set up according to the manufacturer's manual and check for resolution (see Note on Resolution). Scan the region from 2.5 to 15 microns using the parameters in Table 7-1. The sample size should be adjusted so that the most intense peak in the spectrum has a percent transmittance of between 5 to 15 percent. If the spectrum is too weak, more sample must be added, the solvent evaporated, the plates reassembled, and the spectrum rerun as above. If the spectrum is too strong, i.e., peaks with less than 5 percent transmittance, excess sample must be removed by wiping the plates and rerun as above.

7.6.7.2 Procedure for Crystalline Material

The preferable IR sample preparation for crystalline or powdery materials is a KBr pellet. Mix the sample thoroughly to ensure homogeneity. Take about 1 mg of sample and mix with typically 300 mg of KBr powder (amounts can be adjusted to meet specifications of the KBr pellet die used). A small mortar and pestle can be used to mix the sample, but the use of a sample amalgamator or motorized grinder is probably preferable. Add the mixture to the pellet die, assemble and press the pellet according to the manufacturer's instructions, and check for resolution (see Note below). The resulting pellet is placed in the instrument's sample stage, and it is scanned using the parameters in Table 7-1. Normally, the ratio of 1 mg sample to 300 mg KBr powder yields a spectrum of the proper intensity. However, more sample can be added, or the pellet diluted with more KBr, reground, and rerun as required. Excessively thick samples, as evidenced by an opaqueness of the sample pellet or by an extremely low level of transmittance when the sample is placed in the instrument's sample beam, are to be reground, diluted with KBr and re-pelletized. These thick samples will not produce a spectrum with resolution suitable for interpretation and identification of chemical groups.

Table 7-1. Instrument Scanning Parameters

Scan time for 2.5 - 15 microns	10-12 minutes
Scale expansion	1X-10X, as required
Transmittance/absorbance mode switch	Transmittance

Note on Resolution

The instrument settings affecting resolution will vary somewhat with different instrument manufacturers and models. The instrument preparation shall include a test scan using a standard polystyrene film. Comparison of the obtained spectra with an acceptably resolved standard spectra will demonstrate that the instrument is performing acceptably. This resolution check shall be performed at least once each day that samples are analyzed. Figure 7-3 (a) and (b) shows typically acceptable resolutions.

The resulting spectra are interpreted by one with training and experience in this field. Access to the several general and special literature sources on IR interpretation are assumed.

Note on Moisture in Sample

A very broad peak over the area 2.9 to 3.0μ and a moderately strong peak at 6.0μ are generally indicative of water in the sample or in the KBr in the case of a pellet. The pellet should be reground, dried further and then remade before a spectrum is recorded for analysis purposes. A sample on a salt window may need to be dried under a heat lamp before a satisfactory scan can be made. The water spectrum can obscure bands produced by particular functional groups, and can thereby result in an inaccurate spectral interpretation.

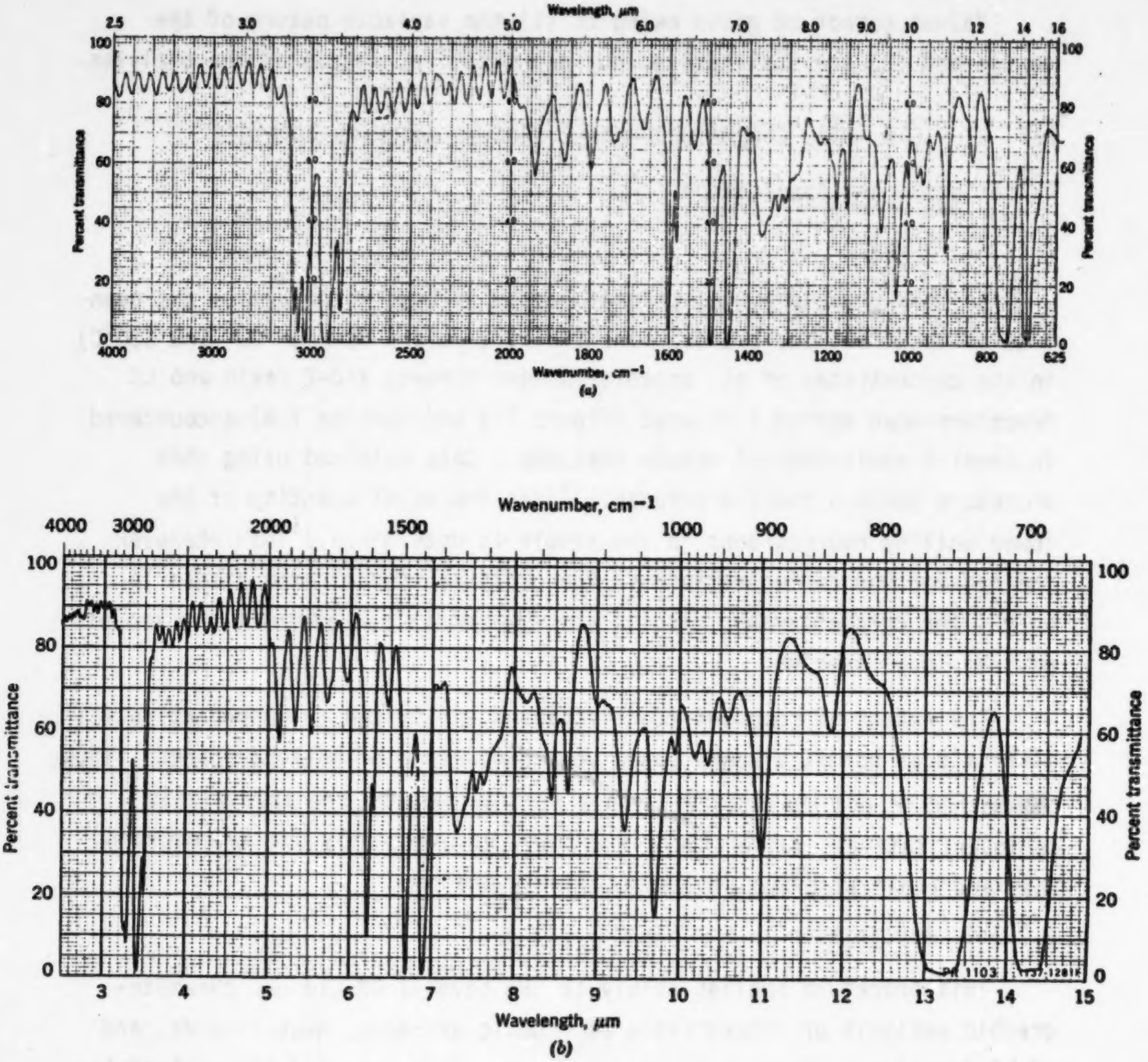

FIGURE 7-3. Standard Polystyrene Film Spectra Showing Acceptable Resolution. (a) Linear in Wave Number (cm^{-1}), (b) Linear in Wave Length (μm)

7.6.8 Calculations

Calculations are not required in this qualitative technique.

7.6.9 Accuracy and Precision

Values cannot be given owing to (1) the variable nature of the sample and (2) the qualitative, not quantitative, nature of the analyses.

7.7 C7 - C16 TOTAL CHROMATOGRAPHABLE ORGANIC MATERIAL ANALYSIS*

7.7.1 Scope and Application

7.7.1.1 Scope

In this procedure, gas chromatography is used to determine the quantity of lower boiling hydrocarbons (boiling points between 90^0 and 300^0C) in the concentrates of all organic solvent rinses, XAD-2 resin and LC fractions—when Method 1 is used (Figure 7-2 and Section 7.8)—encountered in Level 1 environmental sample analyses. Data obtained using this procedure serve a twofold purpose. First the total quantity of the lower boiling hydrocarbons in the sample is determined. Then whenever the hydrocarbon concentrations in the original concentrates exceed 75 $\mu g/m^3$, the chromatography results are reexamined to determine the amounts of individual species.

The extent of compound identification is limited to representing all materials as normal alkanes based upon comparison of boiling points. Thus, the method is not qualitative. In a similar manner, the analysis is semiquantitative: calibrations are prepared using only one hydrocarbon. They are replicated but samples routinely are not.

7.7.1.2 Application

This procedure applies solely to the Level 1 C7-C16 gas chromatographic analysis of concentrates of organic extracts, neat liquids, and of LC fractions. Throughout the procedure, it is assumed the analyst has been given a properly prepared sample.

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*TCO analyses of particulate extracts and probe and cyclone rinses were eliminated after March, 1978, by an official U.S. EPA change to Level 1.

7.7.1.3 Sensitivity

The sensitivity of this procedure, defined as the slope of a plot of response versus concentration is dependent on the instrument and must be verified regularly. TRW experience indicates the nominal range is of the order of 77 μV·sec·μl/ng of n-heptane and 79 μV·sec·μl/ng of n-hexadecane. The instrument is capable of perhaps one hundredfold greater sensitivity. The level specified here is sufficient for Level 1 analysis.

7.7.1.4 Detection Limit

The detection limit of this procedure as written is 1.3 ng/μl for a 1 μl injection of n-decane. This limit is arbitrarily based on defining the minimum detectable response as 100 μV·sec. This is an easier operational definition than defining the minimum detection limit to be that amount of material which yields a signal twice the noise level.

7.7.1.5 Range

The range of the procedure will be concentrations of 1.3 ng/μl and greater.

7.7.1.6 Limitations

Reporting Limitations. It should be noted that a typical environmental sample will contain compounds which: (a) will not elute in the specified boiling ranges and thus will not be reported and/or (b) will not elute from the column at all and thus will not be reported. Consequently, the organic content of the sample as reported is a lower bound and should be regarded as such.

Calibration Limitations. Quantitation is based on calibration with n-decane. Data should therefore be reported as, e.g., mg C8/m^3 as n-decane. Since response varies linearly with carbon number (over a wide range the assumption may involve a 20% error), it is clear that heptane (C7) detected in a sample and quantitated as decane will be overestimated. Likewise, hexadecane (C16) quantitated as decane will be underestimated. From previous data, it is estimated the error involved is on the order of 6-7%.

Detection Limitations. The sensitivity of the flame ionization detector varies from compound to compound. However, n-alkanes as a class have a greater response than other classes. Consequently, using an n-alkane as a calibrant and assuming equal responses of all other compounds tends to give low reported values.

7.7.2 Summary of Method

A 1 ml aliquot of all 10 ml concentrates is disbursed for gas chromatography analysis. When Method 1 is followed (see Section 7.2), LC fractions are also disbursed for GC-TCO analysis. With boiling point-retention time and response-amount calibration curves, the data (peak retention times and peak areas) are interpreted by first summing peak areas in the ranges obtained from the boiling point-retention time calibration. Then, with the response-amount calibration curve, the area sums are converted to amounts of material in the reported boiling point ranges.

After the instrument is set up, the boiling point-retention time calibration is effected by injecting a mixture of n-C7 through n-C16 hydrocarbons and operating the standard temperature program. Response-quantity calibrations are accomplished by injecting n-decane in n-pentane standards and performing the standard temperature program.

7.7.3 Definitions

- GC - Gas chromatography or gas chromatograph
- C7-C16 n-alkanes: heptane through hexadecane
- GCA temperature program: 4 minutes isothermal at 60°C, 10°C/min from 60° to 220°C
- TRW temperature program: 5 minutes isothermal at room temperature, then program from 30°C to 250°C at 15°C/min.

7.7.4 Sample Handling and Preservation

After concentration of organic extracts and rinses to 10 ml (Section 7.4), a 1 ml aliquot is taken for both this analysis and possible subsequent GC/MS analysis (Section 7.10) and set aside in the sample bank.

For each GC-TCO analysis, obtain the sample sufficiently in advance to allow it to warm to room temperature. For example, after one analysis is started, return that sample to the sample bank and take the next sample.

7.7.5 Apparatus

7.7.5.1 Gas Chromatograph

This procedure is intended for use on a Varian 1860 gas chromatograph, equipped with dual flame ionization detectors and a linear temperature programmer. Any equivalent instrument can be used provided that electrometer settings, etc., be changed appropriately.

7.7.5.2 Gases

- Helium - minimum quality is reactor grade. A 4A or 13X molecular sieve drying tube is required. A filter must be placed between the trap and the instrument. The trap should be recharged after every third tank of helium.
- Air - zero grade air is satisfactory.
- Hydrogen - zero grade.

7.7.5.3 Syringe

Syringes are Hamilton 701N, 10 μl, or equivalent.

7.7.5.4 Septa

Septa will be of such quality as to produce very low bleed during the temperature program. An appropriate septum is Supelco Microsep 138, which is Teflon backed. If septum bleed cannot be reduced to a negligible level, it will be necessary to install septum swingers on the instrument.

7.7.5.5 Recorder

The recorder for this procedure must be capable of no less than 1 mV full-scale display, a 1 second time constant, and 0.5 inch per minute chart rate.

7.7.5.6 Integrator

An integrator is required. Peak area measurement by hand is satisfactory but too time-consuming. If manual integration is required, the height times width at half height method is used.

7.7.5.7 Columns

- Preferred column - 6 ft x 1/8 in. O.D. stainless steel column of 10% OV-101 on 100/120 mesh Supelcoport.
- Alternate column - 6 ft x 1/8 in. O.D. stainless steel column of 10% OV-1 (or other silicon phase) on 100/120 mesh Supelcoport.

7.7.5.8 Syringe Cleaner

Hamilton syringe cleaner or equivalent connected to a suitable vacuum source.

7.7.6 Reagents

- Pentane - "Distilled-in-Glass"® or "Nanograde"® for standards and for syringe cleaning.
- Methylene chloride - "Distilled-in-Glass"® or "Nanograde"® for syringe cleaning.

7.7.7 Procedures

7.7.7.1 Setup and Checkout

Each day, the operator will verify the following:

1. Supplies of carrier gas, air and hydrogen are sufficient, i.e., each tank contains > 100 psig.
2. After replacing any gas cylinder, all connections leading to the chromatograph will be leak checked.
3. The carrier gas flow rate is 30 ±2 ml/min; the hydrogen flow rate is 30 ±2 ml/min; and the air flow rate is 300 ±20 ml/min.
4. Verify the electrometer is functioning properly.
5. Verify recorder and integrator are functioning properly.
6. Leak check the septa. Leak checking is effected by placing the soap bubble flow meter inlet tube over the injection port adaptors. Septa are replaced after no more than 20 injections.
7. Obtain list of samples to be run.

7.7.7.2 Retention Time Calibration

To obtain the temperature ranges for reporting the results of the analyses, the chromatograph is given a normal boiling point-retention time calibration. The n-alkanes, their boiling points, and data reporting ranges are given in the table below.

	NBP, °C	Reporting Range, °C	Report As
n-heptane	98	90-110	C7
n-octane	126	110-140	C8
n-nonane	151	140-160	C9
n-decane	174	160-180	C10
n-undecane	194	180-200	C11
n-dodecane	214	200-220	C12
n-tridecane	234	220-240	C13
n-tetradecane	252	240-260	C14
n-pentadecane	270	260-280	C15
n-hexadecane	288	280-300	C16

Preparation of Standards. Preparing a mixture of the C7-C16 alkanes is required. There are two ways: (1) there are standards kits (Polyscience Kit) in which there are bottles of mixtures of selected n-alkanes which may be combined to produce a C7-C16 standard; and (2) there are bottles of the individual C7-C16 alkanes from which accurately known volumes may be taken and be combined to give a C7-C16 mixture.

Procedure (Depends on Instrument Used)

1. The programmer upper limit is set at 250°C. If this setting does not produce a column temperature of 250°C, find the correct setting.

2. The programmer lower limit is set at 30°C.
3. Verify the instrument and samples are at room temperature.
4. Inject 1 µl of the n-alkane mixture.
5. Start the integrator and recorder.
6. Allow the instrument to run isothermally at room temperature five minutes.
7. Shut the oven door.
8. Change mode to Automatic and start the temperature program.
9. Repeat steps 1-9 a sufficient number of times so that the relative standard deviation of the retention times for each peak is <5%.

To attain the required retention time precision, both the carrier gas flow rate and temperature program specifications must be observed.

This calibration is performed at the start of an analytical program. The mixture is chromatographed at the start of each day.

7.7.7.3 Response Calibration

For the purposes of a Level 1 analysis, response-quantity calibration with n-decane is adequate. A 10 µl volume of n-decane is injected into a tared 10 ml volumetric flask. The weight injected is obtained and the flask is diluted to the mark witn n-pentane. This standard contains about 730 ng n-decane per µl n-pentane. The exact concentration depends on temperature, so that a weight is required. Two serial tenfold dilutions are made from this standard, giving standards at about 730, 73, and 7.3 ng n-decane per µl n-pentane, respectively.

Procedure

1. Verify instrument is set up properly.
2. Set electrometer at 1×10^{-10} A/mV.
3. Inject 1 µl of the highest concentration standard.

4. Run standard temperature program as specified above.

5. Clean syringe.

6. Make repeated injections of all three standards until the relative standard deviations of the areas of each standard is ≤5%.

7. This calibration is performed at the start of an analytical program and monthly thereafter. The most concentrated standard is injected once each day. Any change in calibration necessitates a full recalibration with new standards. Standards are stored in the refrigerator locker and are made up monthly.

7.7.7.4 Sample Analysis Procedure

Apparatus

- Gas chromatograph set up and working.
- Recorder, integrator working.
- Syringe and syringe cleaning apparatus.
- Parameters: Electrometer setting is 1 x 10^{-10} A/mV; recorder is set at 0.5-in/min and 1 mV full-scale.

1. Label chromatogram with the date, sample number, etc.
2. Inject sample.
3. Start integrator and recorder.
4. After isothermal operation for 5 minutes, begin temperature program.
5. Clean syringe.
6. Return sample; obtain new sample.
7. When analysis is finished allow instrument to cool. Turn chromatogram and integrator output and data sheet over to data analyst.

7.7.7.5 Syringe Cleaning Procedure

1. Remove plunger from syringe.
2. Insert syringe into cleaner; turn on aspirator.

3. Fill pipet with pentane; run pentane through syringe.
4. Repeat with methylene chloride from a separate pipet.
5. Flush plunger with pentane followed by methylene chloride.
6. Repeat with methylene chloride.

7.7.8 Sample Analysis Decision Criterion

The data from the TCO analyses of organic extract and rinse concentrates are first used to calculate the total concentration of C7-C16 hydrocarbon-equivalents (Section 7.7.9) in the sample with respect to the volume of air actually sampled, i.e., $\mu g/m^3$. On this basis, a decision is made both on whether to calculate the quantity of each n-alkane equivalent present and on which analytical procedural pathway will be followed. (See Figure 7-2). If the total organic content is great enough to warrant continuing the analysis -- $>500\ \mu g/m^3$ -- a TCO of less than 75 $\mu g/m^3$ will require only LC fractionation and gravimetric determinations and IR spectra to be obtained on each fraction. If the TCO is greater than 75 $\mu g/m^3$, then the first seven LC fractions of each sample will be reanalyzed using this same gas chromatographic technique.

7.7.9 Calculations

7.7.9.1 Boiling Point - Retention Time Calibration

The required data for this calibration are on the chromatogram and on the data sheet. The data reduction is performed as follows:

1. Average the retention times and calculate relative standard deviations for each n-hydrocarbon.
2. Plot average retention times as abscissae versus normal boiling points as ordinates.
3. Draw in calibration curve.
4. Locate and record retention times corresponding to boiling ranges 90-110, 110-140, 140-160, 160-180, 180-200, 200-220, 220-240, 240-260, 260-280, 280-300°C (See example in Figure 7-4).

7.7.9.2 Response-Amount Calibration

The required data for this calibration are on the chromatogram and on the data sheet. The data reduction is performed as follows:

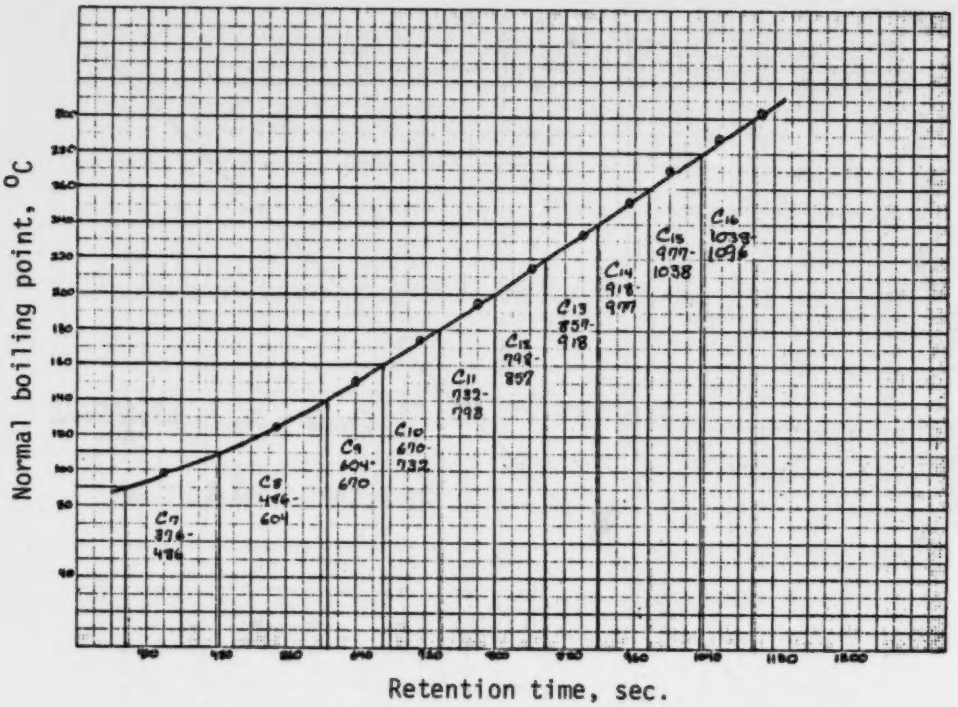

Figure 7-4. Retention Times Versus Normal Boiling Points For C7-C16 Hydrocarbons

1. Average the area responses of each standard and calculate relative standard deviations.

2. Plot response (μV.sec) as ordinate versus ng/μl as abscissa. (See example in Figure 7-5.)

3. Draw in the curve. Perform last squares regression and obtain slope (μV.sec.μl/ng).

7.7.9.3 Total C7-C16 Hydrocarbons Analysis

The required data for this calculation are on the chromatogram and on the data sheet. The data reduction is performed as follows:

1. Sum the areas of all peaks within the retention time range of interest.

2. Convert this area (μV.sec) to ng/μl by dividing by the weight response for n-decane (μV.sec.μl/ng).

3. Multiply this weight by the total concentrate volume (10 ml) to get the weight of the C7-C16 hydrocarbons in the sample.

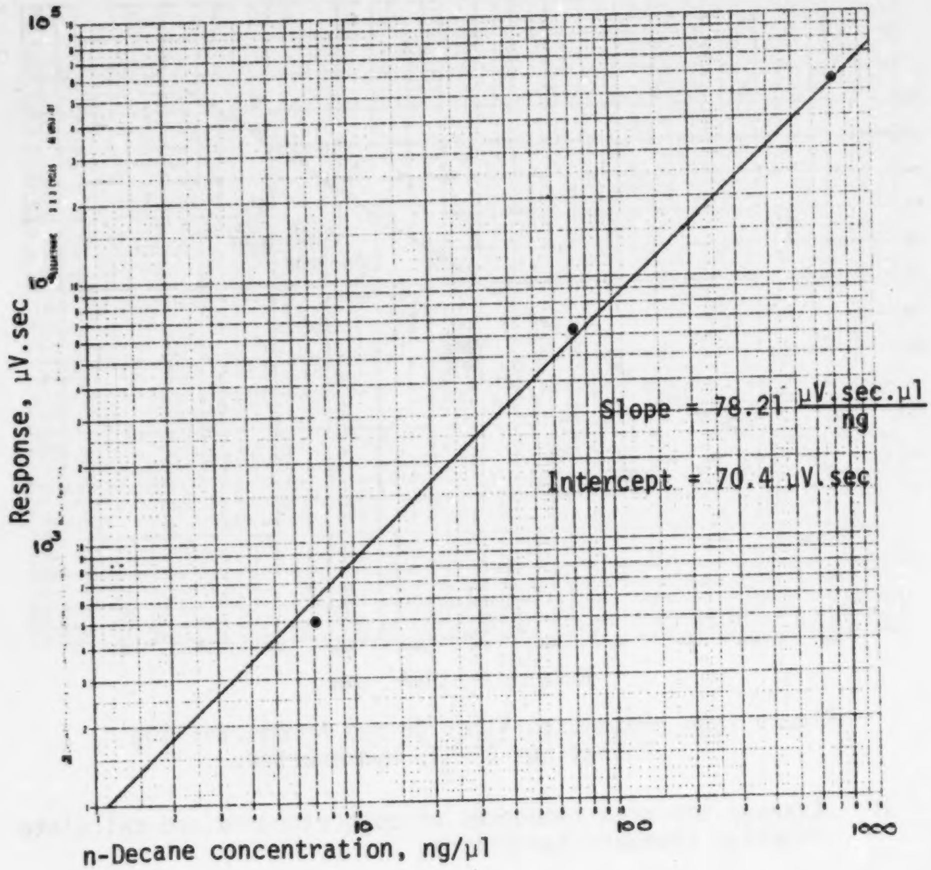

Figure 7-5. Calibration of FID-GC With n-Decane

4. Using the volume of gas sampled or the total weight of sample acquired, convert the result of step 3 above to µg/m^3.

5. If the value of total C7-C16 hydrocarbons from step 4 above exceeds 75 µg/m^3, calculate individual hydrocarbon concentration in accordance with the instructions in Section 7.7.10.4 below.

7.7.9.4 Individual C7-C16 n-Alkane Equivalent Analysis

The required data from the analyses are on the chromatogram and on the data sheet. The data reduction is performed as follows:

1. Sum the areas of peaks in the proper retention time ranges.
2. Convert areas (µV.sec) to ng/µl by dividing the proper weight response (µV.sec.µl/ng).
3. Multiply each weight by total concentrate volume (10 ml) to get weight of species in each range in the sample.
4. Using the volume of gas sampled on the total weight of sample acquired, convert the result of step 3 above to $\mu g/m^3$.

A sample chromatogram is quantitated in Figure 7-6.

7.7.10 Precision and Accuracy

Even relatively comprehensive error propagation analysis is beyond the scope of this procedure. With reasonable care, peak area reproducibility of a standard should be of the order of 1% RSD. The relative standard deviation of the sum of all peaks in a fairly complex waste might be of the order of 5-10%. Accuracy is more difficult to assess. With good analytical technique, accuracy and precision should be of the order of 10-20%.

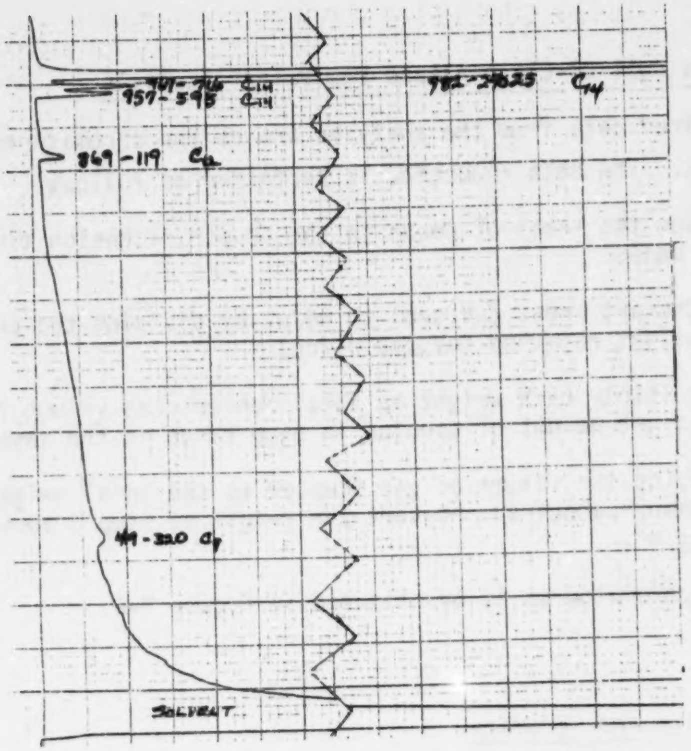

Figure 7-6. Sample Chromatogram With Retention Times and Peak Areas Noted

Example Calculations

1. Sum the peak areas:

$$\text{Total Area} = 320 + 119 + 595 + 716 + 24025$$

$$= 25775 \ \mu\text{V.sec}$$

2. Convert area to concentration by dividing by weight response of n-decane

$$\frac{\text{ng}}{\mu\text{l}} = \frac{25775 \ \mu\text{V.sec}}{78.21 \ \mu\text{V.sec.}\mu\text{l/ng}}$$

$$= 329.6 \ \frac{\text{ng}}{\mu\text{l}}$$

3. Calculate weight of species in concentrated sample

$$\text{Weight} = 329.6 \ \frac{\text{ng}}{\mu\text{l}} \times 10 \text{ ml} \times \frac{10^3 \ \mu\text{l}}{\text{ml}} \times \frac{\mu\text{g}}{10^3 \text{ ng}}$$

$$= 3.30 \times 10^3 \ \mu\text{g}$$

4. Calculate concentration of species in original sample

$$TCO = \frac{3.30 \times 10^2 \ \mu g}{30 \ m^3}$$

$$= 1.10 \times 10^2 \ \mu g/m^3$$

Since this sample contains more than 75 $\mu g/m^3$, the individual n-alkane equivalents will need to be calculated.

1. Sum the peak areas in the proper retention time ranges:

$C7 = 320 \ \mu V.sec$

$C12 = 119 \ \mu V.sec$

$C14 = 595 + 716 + 24025 = 25336 \ \mu V.sec$

2. Convert area to concentration by dividing by weight response of proper n-alkane

$$ng/\mu l \ C7 = \frac{320 \ \mu V.sec}{77.74 \ \mu V.sec.\mu l/ng} = 4.1$$

$$ng/\mu l \ C12 = \frac{119 \ \mu V.sec}{78.40 \ \mu V.sec.\mu l/ng} = 1.5$$

$$ng/\mu l \ C14 = \frac{25336 \ \mu V.sec}{78.53 \ \mu V.sec.\mu l/ng} = 323$$

3. Calculate weight of each species in concentrated sample

$$C7 = 4.1 \frac{ng}{\mu l} \times 10 \ ml \times 10^3 \frac{\mu l}{ml} \times 10^{-3} \frac{\mu g}{ng} = 41 \ \mu g$$

$$C12 = 1.5 \frac{ng}{\mu l} \times 10 \ ml \times 10^3 \frac{\mu l}{ml} \times 10^{-3} \frac{\mu g}{ng} = 15 \ \mu g$$

$$C14 = 323 \frac{ng}{\mu l} \times 10 \ ml \times 10^3 \frac{\mu l}{ml} \times 10^{-3} \frac{\mu g}{ng} = 3.2 \times 10^3 \ \mu g$$

4. Calculate concentration of each species in original sample

$$C7 = \frac{41 \ \mu g}{30 \ m^3} = 1 \mu g/m^3$$

$$C12 = \frac{15 \ \mu g}{30 \ m^3} = 0.5 \ \mu g/m^3$$

$$C14 = \frac{3.2 \times 10^3 \ \mu g}{30 \ m^3} = 107 \ \mu g/m^3$$

7.8 LIQUID CHROMATOGRAPHIC SEPARATIONS

7.8.1 Scope and Application

7.8.1.1 Scope

This procedure is designed to give a separation of a sample into seven reasonably distinct classes of compounds.

7.8.1.2 Application

This procedure applies to Level 1 analyses and to SASS train samples which contain a minimum of 12 mg of nonvolatile organics. Sample weights from bulk liquids and solids will need to be evaluated on a case-by-case basis.

7.8.1.3 Sensitivity

As defined, this procedure will permit the analyst to measure as low as 1 μg of residue.

7.8.1.4 Detection Limit

The detection limit is 0.1 mg of residue.

7.8.1.5 Range

Samples may range from 9 to 300 mg. The optimum size is considered to be 100 mg.

7.8.1.6 Limitations

Compounds of too high polarity or molecular weight will not be eluted from the column since this procedure is a compromise between cost and data acquisition. Also, compounds of too low molecular weight may be evaporated along with the sample solvent during sample preparation.

Classes of compounds may be observed in more than one fraction as a result of the limited fractionating capacity of this chromatographic procedure.

7.8.2 Summary of Method

A sample weighing from 9 to 100 mg is placed on a silica gel liquid chromatographic column. A series of seven eluents are employed to separate the sample into nominally eight distinct classes of compounds for further analyses.

Depending on the TCO level in the concentrated sample, the fractions may be analyzed by the TCO procedure (Section 7.7) for information on the mass of material present in each fraction. These data supplement the gravimetric and infrared analyses which are performed on all fractions (Sections 7.5 and 7.6).

7.8.3 Definitions

7.8.4 Sample Handling and Preservation

The traveler for this analysis will specify the volume of concentrated extract to be taken to give an appropriate weight of material for the separation. This specific volume is withdrawn with a graduated pipet. Then the sample is returned to storage.

7.8.5 Apparatus

- Column: Water jacketed 200 mm x 10.5 mm i.d. glass column with Teflon stopcock.
- Absorbent: Davison Silica Gel, 60-200 mesh, Grade 950.
- Graduated cylinders: 25 ml and 10 ml.
- Volumetric Flasks: One 25 ml and six 10 ml, precleaned.
- Beakers: 10 and 50 ml.
- Miscrospatula.
- Pipet: 1 ml, Class A.
- Liquid scintillation vials.
- Disposable pipets.
- Glass Wool: Extracted 24 hours with methylene chloride in Soxhlet apparatus.
- Funnel.

7.8.6 Reagents

Solvents are all Distilled-in-Glass®, quality.

- Cyclopentane
- Eluents

Eluents	Amounts Collected
1) pentane	25 ml
2) 20% CH_2Cl_2/pentane	10 ml
3) 50% CH_2Cl_2/pentane	10 ml
4) CH_2Cl_2	10 ml
5) 5% CH_3OH/CH_2Cl_2	10 ml
6) 20% CH_3OH/CH_2Cl_2	10 ml
7) 50% CH_3OH/CH_2Cl_2	10 ml

7.8.7 Decision Criteria for Technique to be Used in Performing LC Separations

As indicated in Figure 7.2, two distinct analytical procedures may be used in the performance of LC fractionations and subsequent analyses. The selection of the pathway "Method 1" or "Method 2" will be based on the results of gravimetric and TCO determinations on the concentrated organic sample (Sections 7.5 and 7.7). For a LC separation to be required, the total organic content of the total, original sample must exceed 500 $\mu g/m^3$. Method 2 is used whenever the volatile hydrocarbon content determined by the TCO analysis is low -- less than 10% of the total. Method 1 is used whenever the volatile materials content is in excess of 10% of the total.

The first difference between Method 1 and Method 2 is in the method of preparing the sample for introduction onto the LC column. In Method 2, where there are few volatile substances, a simple, direct solvent evaporation step is sufficient. In Method 1, however, care must be taken to preserve all the lower boiling components for the LC separation and subsequent analyses. Therefore, a solvent exchange step has been incorporated to transfer the sample from methylene chloride to the non-polar solvent cyclopentane. In addition, when Method 1 is used, a TCO analysis will be performed on the seven fractions. Since the TCO of the original sample is a significant portion of the total organic content, it is important to know more about the types of volatile compounds present.

7.8.8 Procedure

The volume of samples expected during the Source Assessment program means that a reasonable number of LC separations will be performed. Six columns are the maximum that will be operated by any single analyst. Of these six columns, one will be a blank, unless experience shows the blank is reproducible. Then the blank may be run with every second or third set of columns.

The data to be obtained and recorded are:

- Weight of sample added to column.
- Weights of all fractions as determined in the TCO procedure.
- Weights of fractions after they have been evaporated in glass beakers to constant weight.

7.8.8.1 Sample Preparation by Solvent Exchange (Method 1)

1. Obtain volume of sample extract calculated to contain 9 to 100 mg of solute: 9 mg is the minimum usable quantity, and 100 mg is the optimum weight.
2. Pipet the extract into a K-D receiver graduated centrifuge tube.
3. Add 200 mg of cleaned, freshly activated silica gel (Section 7.8.8.3) to the sample and mix thoroughly using a microspatula.
4. Protecting the container opening with a small ribbed watch glass or cleaned aluminum foil, set it in a hood and allow the solvent to evaporate at room temperature to a 1 ml volume.
5. Add 1 ml cyclopentane and mix by gentle agitation.
6. Again allow the solvent to evaporate to a 1 ml volume.
7. Repeat steps 5 and 6.
8. The cyclopentane and silica gel are now ready for transfer to the top of a previously prepared LC column. A Pasteur pipet is suggested to handle this material.
9. Rinse the sample container used with another 0.5 ml of cyclopetane, then transfer this solvent to the top of the LC column.

7.8.8.2 Method 2 Sample Preparation, Evaporation to Dryness

1. Pipet or accurately measure a volume of sample extract calculated to give either the optimum weight, 100 mg, or a weight not less than 9 mg. Calculate the exact weight from the gravimetric determination (Section 7.5).

2. Obtain a precleaned and labeled beaker of at least 30% greater capacity than the required volume of sample. Pipet the sample into the beaker, cover loosely with a watch glass, place in a fume hood and evaporate the solvent nearly to dryness.

3. Add 0.5-1.0 g of freshly activated silica gel (Section 7.8.8.3) to the sample container and mix thoroughly with sample using a microspatula.

4. Add 5 ml cyclopentane and allow the sample to evaporate again to about 1 ml.

5. Transfer the 1 ml mixture of cyclopentane and silica gel via a Pasteur pipet to the top of the prepared LC column.

6. Rinse the receiver with another 0.5 ml cyclopentane and transfer this volume of solvent to the top of the LC column.

7.8.8.3 Cleaning and Activation of Silica Gel

The silica gel is cleaned by extracting it in a Soxhlet apparatus for 24 hours using the sequence of solvents methanol, methylene chloride, and finally pentane. The apparatus and procedure are as follows:

Apparatus

- Soxhlet extractor with glass thimble and condenser.
- Boiling flask with stopper of a size to match the Soxhlet extractor.
- Heating mantle to fit boiling flask and variable transformer or steam bath.

Reagents

- Methanol, Distilled-in-Glass®
- Methylene chloride, Distilled-in-Glass®
- n-Pentane, Distilled-in-Glass®

Procedure

a) Place the silica gel to be extracted in the glass thimble.

b) Fill the boiling flask half-full with methanol.

c) Fit extractor onto flask and insert thimble into extractor and add more solvent to fill the extractor. Complete assembly by attaching condenser and clamping entire apparatus in position in heating mantle.

d) Heat the flask sufficiently to produce one discharge cycle about every ten to fifteen minutes. Extract each sample for 24 hours. During the first cycle, check the seating of the ground glass joints by rotating the joints while pushing the condenser/extractor and extractor/flask together. Check for solvent loss periodically throughout the extraction and add solvent as necessary.

e) At the completion of the extraction, allow the extractor to cool. Remove the condenser. Pull out the thimble allowing any remaining solvent to drain into the extractor and siphon off any solvent in the extractor into the boiling flask. Remove the extractor.

f) Discard the solvent.

g) Repeat the process with methylene chloride and then with n-pentane.

h) When the extraction is completed, transfer the silica gel to either a large shallow pan or a rotary evaporator to dry.

Activate the solvent free silica gel by heating at 110°C for two hours in a suitable oven. Then cool and store in a desiccator.

7.8.8.4 Column Preparation

1. Plug the outlet of the precleaned column with glass wool. Dry pack the column with 6.5 grams of freshly activated silica gel. For freshly activated silica gel, this weight occupies 9 ml in a 10-ml graduated cylinder. Tap the column briefly with the microspatula to compact the bed.

2. Take a 50 ml volume of pentane and pour it through the column until the bed is homogeneous, free of any cracks, and free of any air bubbles. Continue pentane flow until the 50 ml volume is used. The pentane level should be at the top of the bed.

   NEVER ALLOW THE TOP OF THE BED TO GO DRY.

3. Keep the column cool to prevent air bubbles and gel cracks. Inlet water temperature to the water jacket should be 18-22°C. If water jackets are not available, wrap the column with acetone moistened towels. (Do not allow any acetone to drip into sample receivers.)

7.8.8.5 Elution of Sample

1. Position a 25-ml volumetric flask as a receiver under the column. Transfer the prepared sample onto the column. Rinse the sample container into the column three times with 1 ml of pentane each time. Begin adding 22 ml of pentane, and start elution at a flow rate not greater than 1 ml/min. Collect 22 ml of pentane, adding more to the column if necessary. Do not allow pentane level to go below the top of the bed.

2. When 22 ml of pentane are collected, the pentane level is at the top of the bed. Take 10 ml of Eluent No. 2 in a graduated cylinder. Use 2 ml to rinse the sample container into the column. Add the remaining 8 ml of Eluent No. 2 to the column and start eluting. Collect 3 ml more of eluent in the 25 ml receiver, then stop elution. This is the first fraction. Label this and succeeding fractions as they are collected.

3. After the first fraction has been collected, place a 10 ml volumetric flask under the column as receiver. Start elution and collect 10 ml of Fraction 2, adding small amounts of Eluent No. 2, 20% CH_2Cl_2 in pentane, as necessary. At the end of collection, the solvent level must be at the top of the bed. This is fraction No. 2.

4. Replace the receiver with another 10-ml volumetric flask. Take 10 ml of Eluent No. 3, 50% CH_2Cl_2/pentane in a graduated cylinder. Rinse sample container into the column with 2 ml of solvent. Start elution and add remaining solvent. Collect 10 ml of Fraction No. 3, adding small amounts of the solvent if necessary. Again, at the end of collection, the solvent level must be at the top of the bed.

5. Repeat step 4 with the remaining eluents:
   - CH_2Cl_2, 10 ml
   - 5% CH_3OH/CH_2CL_2, 10 ml
   - 20% CH_3OH/CH_2Cl_2, 10 ml
   - 50% CH_3OH/CH_2CL_2, 10 ml
6. Reserve 1 ml aliquots of each fraction for TCO analyses by transferring 1 ml with a pipet to a liquid scintillation vial. Label these vials with the sample number.
7. In the area specified for solvent evaporation, quantitatively transfer sample Fractions 1-7 into precleaned, tared, and labeled glass beakers. Final quantitative transfer is achieved by rinsing each sample fraction receiver two times with 2-ml volumes of methylene chloride.
8. The solvents are allowed to evaporate. When all fractions appear dry, weigh twice daily until weights stabilize to within ±0.002 mg.
9. After final weights are obtained, store the beakers in a disiccator and return to sample controller.

7.8.9 Calculations

Data collected are:

- Weights of sample when constant weight was achieved.
- Weights of the fractions when constant weights were achieved.
- Weights of the blank fractions when constant weights were achieved.
- Weights of volatile materials in the fractions from TCO analyses.

The weights of the sample fractions are corrected for the weights of corresponding blank fractions before being transmitted to program management. For internal use, the percentage distribution in the fractions will also be calculated.

7.9 LOW RESOLUTION MASS SPECTROMETRIC ANALYSIS

7.9.1 Scope and Application

7.9.1.1 Scope

This procedure is a survey analysis used to determine compound types in an organic sample or in an LC fraction of a sample. The analyst is specifically searching for hazardous compounds or compounds which may be generally considered toxic. Examples are aromatic hydrocarbons and chlorinated organics. Analysis using different sample ionizing parameters results in molecular weight data, which, combined with IR and sample source data, can provide specific compound identifications on a "most probable" basis.

The mass spectrometer (MS) used in this procedure should have sufficient sensitivity such that 1 nanogram or less presented to the ionizing chamber will result in a full spectrum with a signal ratio of 10:1. A dynamic range of 250,000 or better should be achievable.

7.9.1.2 Detection Limit

The detection limit for a specific compound related to the size of an air sample or liquid sample will vary widely depending on the types and quantities of the species in the mixture. This is because of interfering effects in the spectrum caused by multiple compounds. The impact of this interference may be reduced by lowering the ionization voltage to produce spectra containing relatively more intense molecular ions.

7.9.2 Summary of Method

Solid samples are placed in a sample cup or capillary for introduction via the direct insertion probe. More volatile samples are weighed into a cuvette for introduction through a batch or liquid inlet system. The probe or cuvette is temperature programmed from ambient temperature to 300°C. Periodic MS scans are taken with a 70 eV ionizing voltage as the sample is volatilized during the program. A lower ionizing voltage range (10-15eV) may be used at the discretion of the operator if the 70eV data are complex. Spectra are interpreted using reference compound spectral libraries, IR data, and other chemical information available on the sample. The results of LRMS analysis give qualitative information on compound types, homologous series and, in some cases, identification of specific compounds. This information is then used to assess the hazardous nature of the sample.

7.9.3 Definitions

- LRMS - Low resolution mass spectrometry. Low resolution means that only unit mass data are typically obtained, i.e., instrument resolution is sufficient to separate and identify peaks differing by one atomic mass unit (AMU).
- LC - Liquid Chromatography
- MS - Mass Spectrometer
- Molecular ion - The unfragmented ionized molecule. This ion provides the molecular weight of the molecule when detected.
- "Most probable" - This term refers to the confidence in a compound identification based upon all chemical and spectroscopic information known about the sample.

7.9.4 Sample Handling and Preservation

Samples are usually residues in aluminum dishes or glass beakers, from which solvents have been removed by evaporation and desiccation. Occasionally, the residue will be somewhat fluid due to the presence of a rather nonvolatile liquid. Samples should be stored in a refrigerator when not in use. All dishes and implements must be carefully washed in warm soapy water, rinsed several times with water followed by pure organic solvents such as hexane, acetone, or methylene chloride and finally dried. Contacting the sample with hands, fingers and other sources of outside contamination must be avoided.

7.9.5 Apparatus

Finnigan - Model 4023 Automated GC/MS

Several other quadrupole or magnetic sector MS instruments, automated or manual, can be used to perform this analysis. Minimum requirements are:

- Resolution sufficient to separate nominal mass peaks from 40 to 1000 AMU

- A solid inlet system (probe)
- A batch inlet system for liquid samples. (This can be the gas chromatograph).
- Variable ionization voltages from 4 eV to at least 70 eV
- Electron multiplier detection system

7.9.6 Reagents

Supplies of the following, pesticide grade, Distilled-in-Glass®, solvents or their equivalents should be kept in 1 or 2 liter quantities. These solvents are used to dissolve and homogenize the sample residues prior to placement in the solid probe capillary. Solvent selection is at the discretion of the operator and is based on knowledge of the sample (e.g., which LC fraction, IR data, solubilities, etc.). The solvents are:

- Pentane
- Methylene Chloride
- Methanol
- Petroleum ether
- Di-ethyl ether

7.9.7 Procedure

7.9.7.1 Instrument Preparation

The procedure assumes that the MS has been activated in accordance with the instrument instruction manual and has been prepared to gather and record data. Briefly, summarized this procedure includes:

- Monitoring all applicable pressures and confirming that proper vacuum levels are being achieved.
- Checking all applicable temperatures and making adjustments as necessary.
- Checking performance of ionizer.
- Optimizing resolution/sensitivity
- Confirming that all electronics associated with data collection are functioning properly.

When all the necessary checks have been performed, proceed with the analysis.

7.9.7.2 Analysis of the Sample

1. Place 1 microgram or less of the sample in a solid probe glass capillary. The sample may be loaded as a solid, however, it is preferable to dissolve the sample in a solvent and load it as a solution. Both techniques, described in steps (a) and (b) below, ensure controlled evaporation of the sample into the ion source. Avoid touching or otherwise contaminating the solid probe tip or the glass capillary. Always wear clean nylon gloves or equivalent when handling the solid probe tip, and use forceps to handle the glass capillaries.

    a. If the sample is in solution, the solvent must be evaporated prior to inserting the sample into the mass spectrometer. Do this by gently heating the glass capillary under a heat lamp or with an appliance such as a hair dryer.

    b. If the sample is inserted as a solid, it may occasionally blow out of the capillary if it is heated too quickly. To prevent this, place the sample at the bottom of the glass capillary and insert a small quantity of silanized glass wool (pyrex) over it.

    CAUTION: Sample size should be 1 μg or less to minimize contamination of the ion source.

2. Place the capillary tube into the end of the solid probe by pushing the retaining spring aside and then releasing it to hold the capillary tube in place.

3. Insert the solid probe tip into the slip vacuum seal at the entrance of the solid inlet and push the solid probe in until the index pin in the guide rod snaps into the hole in the tube.

4. Tighten the slip vacuum seal by turning the black knob clockwise.

5. Evacuate the solid inlet and monitor the inlet pressure. When it has reached 0.04 torr stop the evacuation.

6. Open the solid probe valve by rotating the crank counterclockwise.

7. Depress the locking button on the guide rod, and slowly push in the solid probe to the full length of travel.

8. Connect one end of the solid probe heating cable to the socket in the handle of the probe. Connect the other end of the cable to the connector labeled Program.

9. Prepare the mass spectrometer for acquiring data. Parameters which must be entered into the MS controller include:

   Solid probe temperature – Program rate to be determined

   Mass range – 40-600

   Scan time for mass range – 2 sec

   Scan interval – 50°C

   Record this data in the instrument log book.

10. Set the temperature program controls for a heating interval of ambient to 300°C at the temperature increase rate desired. The rate may be adjusted by the operator at his discretion to control sample sputtering, etc. Depress the Solid Probe Selector push button under the temperature readout to monitor the probe temperature.

11. Start data collection and depress the Solid Probe pushbutton to start the heating cycle. The probe will now heat at the selected rate while MS data is acquired, processed, and stored in the computer.

12. When the probe temperature reaches 300°C, stop data acquisition by pressing the appropriate computer stops. Turn the solid probe heater off and allow the probe to cool. Then disconnect the cable from the probe handle and pull the probe out to the stop. Close the solid inlet valve by turning the handle clockwise. Loosen the slip vacuum seal knob. Push down on the stop pin in the guide rod, and withdraw the probe. Remove the capillary and visually estimate if possible, the amount of sample that has volatilized. Record this estimate as either 0, 25, 50, 75, or 100 percent volatilized.

7.9.8 Data Interruption

The raw data from an LRMS analysis consist of mass spectra recorded on oscillograph recorder paper or computer output from a printer plotter. The data are equivalent and consist of atomic mass units (AMU) on the bottom of the chart (abscissa) and the relative ion intensity on the sides (ordinate). Interpretation of a spectrum is accomplished by utilizing several sources of information. All inputs are considered in making a determination and in estimating the degree of confidence in the spectral assignments. Assistance with interpreting data is available from several sources, including the following:

1. The nature of the sample, e.g., water extract, fuel extract, which of the several liquid chromatography fractions, etc.
2. Results of infrared spectrophotometric analysis on same sample and other chemical information.
3. Published compilations of MS data for standard compounds.
4. Operator experience and skills using correlations between molecular structure and mass spectra as well as the simple ability to recognize spectral features critical to the identification of compound classes or compound group types.

No standardized spectral interpretation procedure is believed to be used by a majority of operators. However, the basic elements of data interpretation are presented below.

1. Study all available information about the sample.
2. Verify that the mass counter is accurate.
3. Study the general appearance of the spectrum, e.g., molecular ion intensities, isotopic abundances as an indication of certain heteroatoms, rings plus double bonds,based on the molecular ion and characteristic ions.
4. Identify neutral species accompanying high mass fragment ion formation.
5. Postulate classes of compounds, and test against reference spectra for the same or similar compounds. If these are not available, spectra predicted from ion decomposition mechanisms may be used. Examine the data from analyses run with the low ionization potentials to check molecular ions.

In the analysis mode where low ionization voltages are used (10-15 eV) the intensity of the peaks caused by molecular ions of "most probable" identified compounds can be examined to provide an estimate of the abundances of identified species. Only an estimate can be given because the production and stability of molecular ions is not equal for all compounds. This type of estimation is significantly more error prone when 70 eV ionization energies are used. The estimation procedure is carried out by normalizing all of the molecular ion peaks and reporting each species as a fraction of the total.

7.9.9 Quantitation of Results

The relative quantity of each compound category identified should be estimated on a scale ranging from 100 (major) to 10 (minor) to 1 (trace). It should be possible to account for nearly all observed species by using a relatively small list of compound categories.

7.10 POLYNUCLEAR ORGANIC COMPOUND ANALYSIS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (POM's by GC/MS)

7.10.1 Scope and Application

7.10.1.1 Scope

This is an analysis method for polynuclear organic materials, particularly the polynuclear aromatic hydrocarbons (PAH) in various environmental samples. Aromatic compounds containing heteroatoms in the condensed rings may also be included in the scope of this analysis. The manner in which the GC/MS data are gathered and stored will enable the operator to search for a list of compounds of interest in a routine manner. The list of compounds can be changed as required.

7.10.1.2 Sensitivity

The GC/MS sensitivity varies with several parameters, including the type of compound, instrument internal cleanliness, resolution of closely eluting peaks, etc. Under "everyday" operating conditions 5 nanograms (ng) eluting in a peak about 5 seconds wide will yield a MS signal with a usable signal-to-noise ratio. A dynamic range of greater than 100,000 is achievable.

7.10.1.3 Detection Limit

There will typically have to be at least 10 μg of any single PAH compound extracted from a sample and concentrated to 10 ml of solution for detection limit of 0.3 $\mu g/m^3$. This presumes a 2:1 dilution for addition of the internal standard, a 10 μl sample injection volume, the typical instrument sensitivity specified above, and the sample preparations described below.

7.10.1.4 Interferences

This analysis is performed using the MS in the Total Ion Monitoring (TIM) mode. In this mode, all ion fragments in a specified mass range are monitored and as a result, all compounds eluting from the GC in detectable quantities can be identified. During the search of the data for POM compounds, non-POM compounds may interfere, especially if they co-elute with a POM. Computerized data reduction techniques, such as ion mapping and selected ion chromatograms, keep these interferences to a minimum. If a discrete list of POMs exists for which to search, then a spectral library of these compounds can be stored in the computer data bank as standards against which sample spectra are compared.

7.10.2 Summary of Method

This is a combined gas chromatography/mass spectrometry (GC/MS) method for qualitative and quantitative POM determinations. Microliter quantities of concentrated sample extracts derived from various samples obtained from the sampling activity are used for this analysis. The extraction and concentration procedures are described in Sections 7.3 and 7.4.

Microliter sized (5-10 μl) samples are injected onto a gas chromatographic column and are separated by the differences in the retention characteristics between the sample components and the column material. As the components elute from the GC column, they are transported via an interface to the ion source of the mass spectrometer (MS). The components are ionized in the MS and the ion fragments mass analyzed in the 40-400 AMU range. The resulting mass spectra are stored by the computerized data system. The computer is used to search the stored spectra for mass fragments common to the POMs of interest. Spectra from the GC peaks suspected to be POMs are examined. If a POM is confirmed, the peak is quantitated using an internal standardization method.

7.10.3 Definitions

GC/MS - gas chromatograph/mass spectrometer

POM - polynuclear organic materials

PAH - polynuclear aromatic hydrocarbons

PCB - polychlorinated biphenyl compounds

AMU - atomic mass unit

IS - internal standard

SIM - selected ion monitoring

TIM - total ion monitoring

7.10.4 Sample Handling and Preservation

These samples are organic solutions resulting from extraction and concentration of envirnomental samples. They are contained in capped or sealed ampoules or vials typically containing 1 to 2 ml. These samples may contain toxic materials and due care shall be used in handling all samples and standards. Gloves and fume hoods are appropriate considerations.

7.10.5 Apparatus

This section specifies the major pieces of apparatus required. A normal complement of glassware and implements is assumed.

7.10.5.1 Automated GC/MS - Finnigan Corporation, Model 4023 or Dupont Dimaspec, Model 321

Other quadrupole or magnetic sector instruments coupled with appropriate computer data systems are available to perform this analysis. Basic required capabilities include:

- Resolution sufficient to obtain unit mass peaks in the range from 40 to at least 400 AMU
- Capability for 2 mm ID packed columns and a sample enrichment device to achieve yields and efficiencies such that the 5 ng total instrument sensitivity is achieved
- Electron multiplier detection system
- Total ion monitoring capability in the 40-400 AMU range

7.10.5.2 Interactive Data System

Capable of gathering and storing TIM data, generating total ion and selected ion chromatograms, library searching, and quantitation.

7.10.5.3 GC Column

Six foot X 2 mm ID glass column containing 3% Dexsil 300 on 100-120 mesh Gas Ghrom Q, Chromosorb WHP, or equivalent.

7.10.5.4 GC Injection Syringes

Ten µl syringes with 0.2 µl graduations.

7.10.5.5 Analytical Balance

Capable of weighing ±0.05 mg.

7.10.6 Reagents

7.10.6.1 Solvents

Supplies of the following solvents, Pesticide Grade, Distilled-in-Glass®, or equivalent should be kept at hand in 1 or 2 liter quantities. These solvents will be used to prepare analytical standards, make dilutions, do solvent exchange or other similar activities as required.

- Toluene
- Pentane
- Methylene chloride
- Methanol
- Acetone
- Hexane

7.10.6.2 Standard Compounds

The following compounds are used for retention time and detection limit determination. This list can be expanded or changed as POMs of interest are added or deleted.

Compound	Molecular Weight
Naphthalene	128
Acenaphthene	159
5,6-Benzoquinilene	179
Dibenzothiophene	184
Fluoranthene	202
Pyrene	202
1,2-Benzanthracene	228
1,2-Benzo[a]pryene	252
1,2,5,6-Dibenzanthracene	278
Coronene	300

7.10.6.3 Internal Standard for Working Standard Mixtures

Weigh out 0.01 g ±0.01 mg of α-chloronaphthalene (making corrections for purity if it is less than 99 percent) and dissolve in toluene contained in a Class A 100 ml volumetric flask. This yields a 100 μg/ml solution.

7.10.6.4 Internal Standard for Unknown Samples

Take 20 ml of the above stock solution by pipet and transfer to a 100 ml volumetric flask. Fill to the mark with toluene and mix well. This yields a 20 μg/ml solution.

Note: Different internal standard stock solution concentrations are required depending on whether the sample is a POM standard or an unknown sample. Care must be taken to use the correct stock solution.

7.10.7 Procedure

The GC/MS sample solutions will be prepared in such a way that the solutions will: 1) be concentrated as much as it practical and 2) contain an internal standard for quantification and checking instrument response. The procedures for these preparations are discussed below.

7.10.7.1 Preparation of the Sample Solutions

The 1 ml aliquot of the 10 ml sample resulting from the Kuderna-Danish concentration of the sample extracts should be contained in a clean Teflon capped vial large enough to hold at least 2 ml. Pipet 1.0 ml of the internal standard solution (7.10.6.4) into the vial and shake well to mix. In practice it is probable that samples will be assigned that do not contain 1 ml. These solutions can be prepared as received without further aliquoting but the volume of internal standard solution to be added to the sample must be equal to the volume of the received sample aliquot.

7.10.7.2 Preparation of POM Standard Solutions

Concentrated stock solutions of the POM compounds of interest shall be made. Ten milligrams of a POM in 50 milliliters of toluene produces a suitable concentration of 200 nanograms per microliter (ng/μl). Portions of these stock solutions can be serially diluted or combined with one another to produce working standard mixtures. The working standard solutions will be made up in 10 ml volumetric flasks. When making the working standard mixtures up to 10 ml volume, 1.00 ml of the internal standard stock solution for working standard mixtures (7.10.6.3) will be added as part of the diluent. This will yield solutions that always contain 10 ng of internal standard per µl solution. These POM standard solutions are subjected to the same instrumental analysis given the unknown samples. Data are collected in the same manner as the unknown samples. The responses of individual POM compounds relative to the internal standard are then calculated as shown in Section 7.10.8.

The stock solutions described above will be stored in a refrigerator or preferably a freezer. The volumetric flasks should be wrapped in plastic to minimize exposure to moisture. Storage life times for these solutions have not been specifically measured but they should remain stable for 6 months. All working mixtures and standards should also be stored in the refrigerator when not in use and should be protected from sunlight and fluorescent lighting. These working solutions should be prepared on a monthly basis.

7.10.7.3 Preparation of the GC/MS Instrument

The gas chromatograph shall be prepared according to the manufacturer's operating manual. Key operating parameters to be used are as follows:

Column - 6 ft. X 2 mm ID glass packed with 3% Dexsil 300 on 100-120 Chromosorb WHP or 100-120 Gas Chrom Q.

Carrier Gas - Helium, zero grade at 30 ml/min.

Oven Temperature - 100° - 295°C programmed at 10°/min (the program may be varied to suit a specific situation).

Injector Temperature - 300°C.

Transfer Lines and Separator - oven 260°C - 280°C.

The mass spectrometer shall be prepared according to the manufacturer's operating manual. Briefly summarized, this procedure includes:

- Monitoring all applicable pressures and confirming that proper vacuum levels are being achieved. Proper levels are specified in the manual

- Checking all applicable temperatures and making adjustments as necessary:

  Ion source block - 200°C

  Manifold containing source,
  electron multiplier etc. - 40°C to 60°C

- Checking performance of ionizer
- Optimizing resolution, sensitivity and proper spectral pattern using a calibrant such as FC-43 and/or Ultramark 443
- Confirming that all electronics associated with data collection are functioning properly.

Important MS parameters to be set are as follows:

Electron energy	70 eV
Ionizing energy	0.2 milliamp
Electron multiplier	Adjusted for optimum signal to noise ratio (1.5 to 2.5 KV)
Sensitivity	10^{-7} amps/volt
Analyzer pressure	5×10^{-6} torr or less

Optimum MS parameters can be varied for different instrument systems. Record parameters in instrument log book.

7.10.7.4 Preparation of Computerized Data Acquisition System

Use the Operating Manual for the data system to select the operating parameters for data collection, storage, and processing time.

Mass range	40 - 400 AMU
Scan function	Up 1.9 seconds Down 0.0 seconds Hold at top 0.0 seconds Hold at bottom 0.1 seconds
Ion abundance threshold	Set to minimize "random ion" noise

7.10.7.5 Starting the Analysis

When all preparations have been completed, inject the sample into the gas chromatograph while it is in the solvent divert mode. At a set time after injction, adjust the solvent divert valve as as to direct the GC effluent into the MS. Start data acquisition according to the preselected parameters. The instrument will then gather and store data over the time interval during which the components of the sample mixture will elute. Analysis will continue for a pre-set time or until the operator intervenes. The system shall be programmed to stop the analysis after enough time has elapsed in order for coronene MW 300 to elute.

7.10.8 Data Processing and POM Quantification

7.10.8.1 Computer Generated Total Ion Chromatogram (TIC)

Direct the data system to reconstruct a total ion chromatogram using the acquired data. The peak heights on the chromatogram shall be standardized so that all are relative to the strongest peak which is maximized at 100% of chart. The purpose of the RGC is to provide the analyst with an overview of the relative number and concentration of compounds in the sample. An example of such a chromatogram is shown in Figure 7-7.

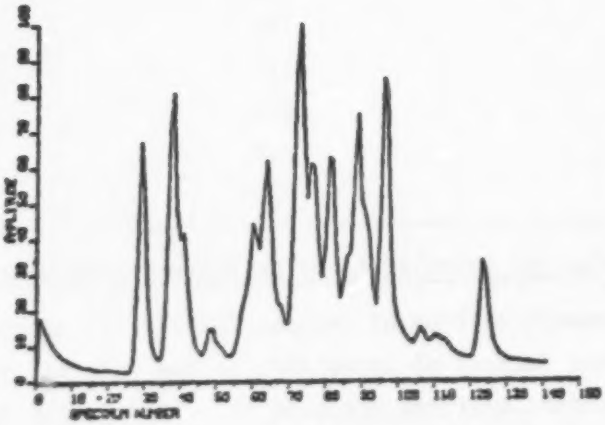

Figure 7-7. Example of a Computer Generated Total Ion Chromatogram

7.10.8.2 Processing Sample Data and Search for POMs

This section summarizes the manner in which stored data are searched for POMs. A reconstructed total ion gas chromatogram is prepared by the computer over the 40 - 400 AMU range. Selected ion mass chromatograms are then prepared using pre-selected m/e values corresponding to the molecular ions of many polynuclear aromatic hydrocarbons. A list of these ions is found in Table 7-2. Table 7-3 is a minimum list of POMs monitored by selected mass chromatograms using the masses in Table 7-2. Many more POMs of similar molecular weights probably exist and will also be detected. Additional POM isomers not listed in Table 7-3, also exist and will be detected. A peak in any of these selected mass chromatograms indicates the potential presence of a POM and must be investigated further by examining the full mass spectra. If a spectrum has an intense molecular ion at one of the m/e values listed in Table 7.2 and if the spectrum is consistent with other POM type compounds, it is assigned to the POM class of compounds. For example, if the mass chromatogram for m/e 128 in the specific ion chromatogram displays peaks, the presence of naphthalene, or azulene, or a similar compound is suspected. The full mass spectrum is taken from an appropriate portion of the chromatogram peak. The spectrum is then examined to confirm the identification.

Table 7-2. Specific Ions Used in PAH Data Search

128	180	242
154	184	252
162	192	256
166	202	278
178	216	300
179	228	302

7.10.8.3 The Use and Calculation of Relative Response Factors

Prior to quantification of unknown POMs, it is necessary to determine the relative response factors of known POMs to the internal standard. To do this, analyze the standard mixtures prepared in 7.10.7.2 with the GC/MS operating under the same conditions used for the unknowns. Calculate the Relative Response Factor (RRF) for each POM in the standard as follows:

$$RRF_{POM} = \frac{A_{POM}}{A_{IS}} \times \frac{C_{IS}}{C_{POM}} \qquad (1)$$

Where

RRF_{POM} = Relative response factor for a POM relative to an internal standard

A_{POM} = Total ion peak area for a POM

A_{IS} = Total ion peak area for the internal standard

Table 7-3. Minimum List of POMs Monitored

Compound Name	MW
Naphthalene	128
Biphenyl	154
Benzindene	166
Fluorene	166
9,10-Dihydro-phenanthrene	180
9,10-Dihydro-anthracene	180
2-Methyl-fluorene	180
1-Methyl-fluorene	180
9-Methyl-fluorene	180
Phenanthrene	178
Anthracene	178
Benzoquinoline	179
Acridine	179
3-Methyl-phenanthrene	192
2-Methyl-phenanthrene	192
2-Methyl-anthracene	192
Fluoranthene	202
Pyrene	202
Benzo[a]fluorene or 1,2-benzofluorene	216
Benzo[b]fluorene or 2,3-benzofluorene	216
Benzo[c]fluorene or 3,4-benzofluorene	216
2-Methyl-fluoranthene	216
4-Methyl-pyrene	216
3-Methyl-pyrene	216
1-Methyl-pyrene	216
Benzo[c]phenanthrene	228
Benzo[ghi]fluoranthene	228
Benzo[a]anthracene	228
Chrysene	228
Triphenylene (9,10 Benzo phenanthrene)	228
4-Methyl-benzo[a] anthracene	242
1-Methyl-chrysene	242
6-Methyl-chrysene	242

(Continued)

Table 7-3. (Continued)

Compound Name	MW
7,12-Dimethyl-benzo[a]anthracene	256
9,10-Dimethyl-benzo[a]anthracene	256
Benzo[f]fluoranthene	252
Benzo[k]fluoranthene	252
Benzo[b]fluoranthene	252
Benzo[a]pyrene	252
Benzo[e]pyrene	252
Perylene	252
1,2,3,4-Dibenzanthracene	278
2,3,6,7-Dibenzanthracene	278
Benzo[b]chrysene	278
Picene	278
Benzo[c]tetraphene	256
Benzo[ghi]perylene	302
Coronene	300
1,2,3,4-Dibenzpyrene	302
1,2,4,5-Dibenzpyrene	302

C_{POM} = Concentration of the POM in the standard mixture.

C_{IS} = Concentration of the internal standard in the standard mixture

7.10.8.4 Quantifying POM Peaks in Sample

Calculate the quantity of each POM in the mass chromatogram as follows:

$$C_{POM} = \frac{A_{POM}}{A_{IS}} \times C_{IS} \times \frac{1}{RRF_{POM}} \times \frac{V_{final}}{V_{as\ received}} \qquad (2)$$

Where

C_{POM} = Concentration (μg/ml) of the POM in the GC/MS prepared sample diluted with IS solution.

A_{POM} = Area of unknown peak.

A_{IS} = Area of internal standard peak.

C_{IS} = Concentration (μg/ml) of internal standard in the sample solution.

RRF_{POM} = Relative response factor of the POM as calculated from Equation 1.

V_{final} = Volume of sample (ml) after addition of internal standard solution.

$V_{as\ received}$ = Volume of sample as received. (Normally an aliquot of the 10 ml total sample after Kuderna-Danish concentration).

7.10.8.5 Automated GC/MS Data Reduction and Quantification

Most of the computer software supplied with state-of-the-art computerized GC/MS systems have automated quantification routines which utilize the internal standardization and the quantification techniques described above. The application of these techniques to routine POM analysis is recommended for qualitative and quantitative accuracy as well as reduced labor requirements.

8.0 INORGANIC ANALYSIS PROCEDURES

8.1 INTRODUCTION

Level 1 inorganic analyses will consist of a Spark Source Mass Spectrometric (SSMS) elemental survey along with specific analyses for mercury and sulfate on all samples, ultimate analysis on fuel oil samples, and ultimate and proximate analyses on all coal samples. Additional analyses for arsenic and antimony will be performed on the APS impinger samples. Fluoride and chloride analyses will also be performed on selected Level 1 sites as directed by the Laboratory Operations Manager. The plan for sample preparation and analysis, as shown in Figure 8-1 and 8-2, includes all possible sample types and procedures. However, all of these samples may not exist for a site, or as a result of applying the decision criteria in Chapter 3, not all analyses will always be performed.

The plan given in Figure 8-1 is applicable to all analyses done before June 1978 and that in Figure 8-2 is applicable after this date. The changes incorporated into Figure 8-2 are the result of either EPA mandated Level 1 changes or directed changes by the project officer based on TRW recommendation. These latter changes are based on initial results of the program and were made to effect cost savings without affecting the quality of the technical output of the program. These changes include:

- Performing all As, Sb, Cl, and F analysis by SSMS where possible.
- Deleting all elemental analysis on all gas fired sites.
- Using fuel analysis to compute elemental emissions in all oil and residual oil fired sites.
- Performing ultimate analyses on fuel oils and ultimate and proximate analyses on all coal.
- Replacing the Parr bomb combustion procedure for XAD-2 resin with an acid extraction procedure. (This procedure is pending)

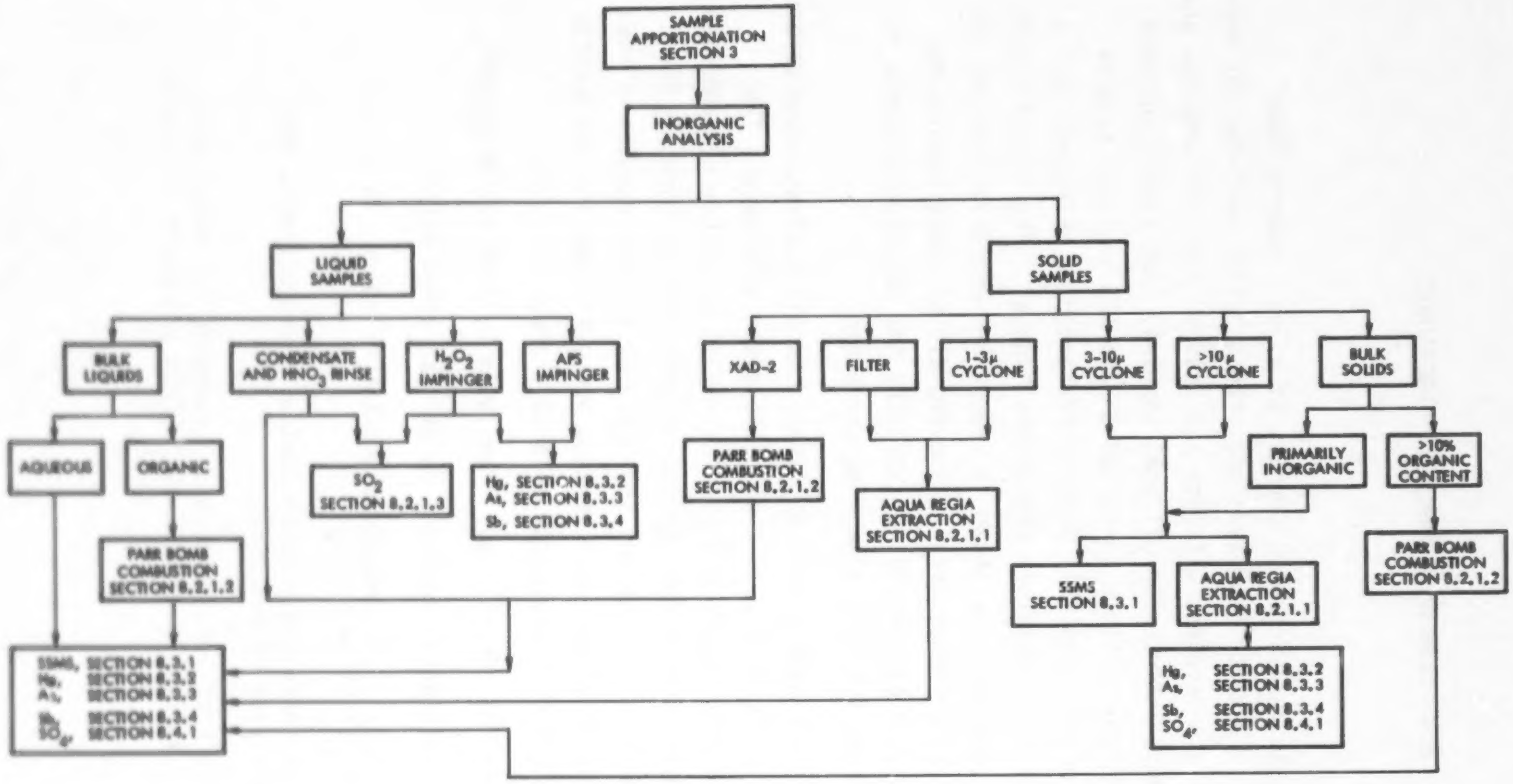
SAMPLE APPORTIONATION SECTION 3
INORGANIC ANALYSIS
LIQUID SAMPLES
SOLID SAMPLES
BULK LIQUIDS
CONDENSATE AND HNO_3 RINSE
H_2O_2 IMPINGER
APS IMPINGER
XAD-2
FILTER
1-3μ CYCLONE
3-10μ CYCLONE
>10μ CYCLONE
BULK SOLIDS
AQUEOUS
ORGANIC
SO_2 SECTION 8.2.1.3
Hg, SECTION 8.3.2
As, SECTION 8.3.3
Sb, SECTION 8.3.4
PARR BOMB COMBUSTION SECTION 8.2.1.2
AQUA REGIA EXTRACTION SECTION 8.2.1.1
PRIMARILY INORGANIC
>10% ORGANIC CONTENT
PARR BOMB COMBUSTION SECTION 8.2.1.2
SSMS SECTION 8.3.1
AQUA REGIA EXTRACTION SECTION 8.2.1.1
PARR BOMB COMBUSTION SECTION 8.2.1.2
Hg, SECTION 8.3.2
As, SECTION 8.3.3
Sb, SECTION 8.3.4
SO_4, SECTION 8.4.1
SSMS, SECTION 8.3.1
Hg, SECTION 8.3.2
As, SECTION 8.3.3
Sb, SECTION 8.3.4
SO_4, SECTION 8.4.1

Figure 8-1. Level 1 Inorganic Analysis Plan (Prior to June 1978)

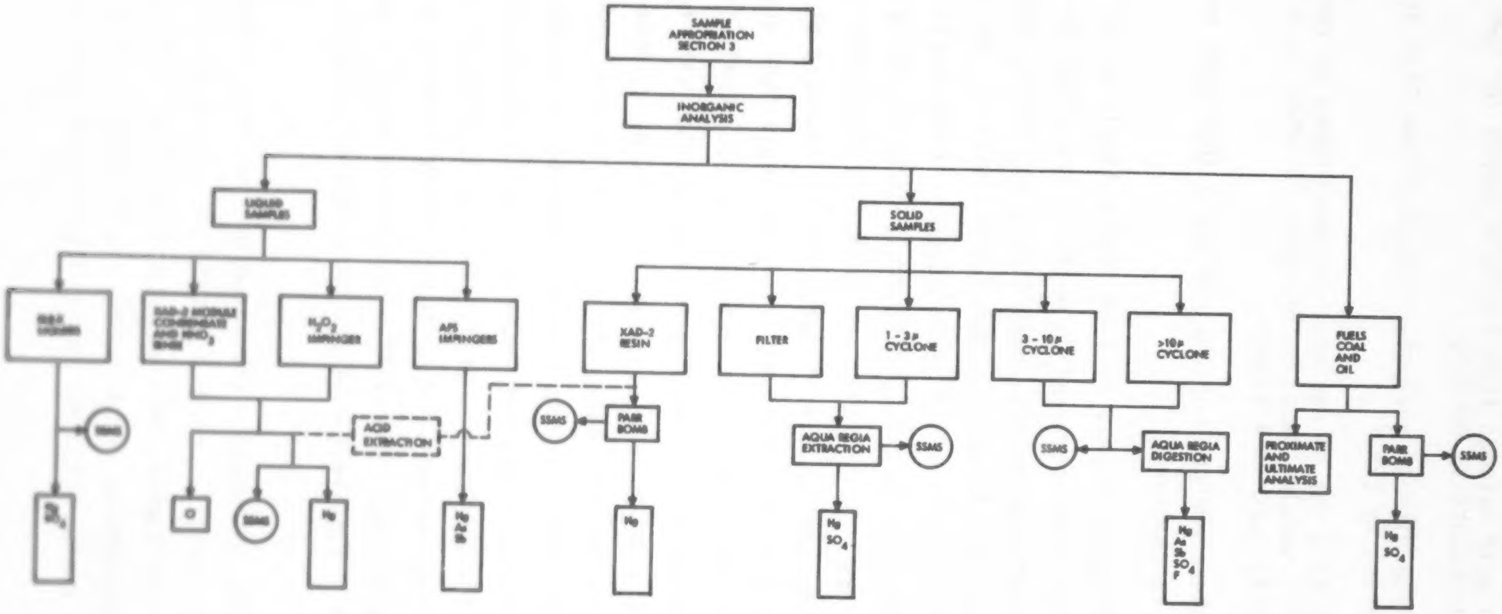
SAMPLE APPROPRIATION SECTION 3
INORGANIC ANALYSIS
LIQUID SAMPLES
SOLID SAMPLES
XAD-2 MODULE CONDENSATE AND HNO$_3$ RINSE
H$_2$O$_2$ IMPINGER
APS IMPINGERS
ACID EXTRACTION
SSMS
Cl
SSMS
Hg
Hg As Sb
XAD-2 RESIN
PARR BOMB
SSMS
Hg
FILTER
1 - 3µ CYCLONE
AQUA REGIA EXTRACTION
SSMS
Hg SO$_4$
3 - 10µ CYCLONE
>10µ CYCLONE
SSMS
AQUA REGIA DIGESTION
Hg As Sb SO$_4$ F
FUELS COAL AND OIL
PROXIMATE AND ULTIMATE ANALYSIS
PARR BOMB
SSMS
Hg SO$_4$

Figure 8-2. Level 1 Inorganic Analysis Plan (After June 1978)

- Combining all samples after the filter into a single sample. This includes the condensate, XAD-2 module rinse, H_2O_2 impinger, and XAD-2 resin acid extract into a single sample for SSMS analysis. (This procedure is pending).
- Elimination of the nitrate analysis because of the lack of any definitive interest by EPA.
- The application of a set of decision criteria based on results of fuel and XAD-2 module composite analyses in order to eliminate unnecessary Hg, As, and Sb analyses.

A discussion of these changes and the rationale that goes into these applications is given in Chapter 3.

Samples for laboratory analysis will be either liquid or solid. Aqueous liquids require only minor preparation which is described in each analytical procedure. Organic materials, both liquid and solid, must be combusted in a Parr oxygen bomb to destroy the organic matrix. An alternative procedure to Parr Bomb combustion for preparation of XAD-2 resin for analysis is included. Approval of this procedure is pending, therefore its use is not yet authorized. Solids that are primarily inorganic (with the exception of glass fiber particulate filters) can be analyzed directly by SSMS, but must be digested with aqua regia for the individual analyses. Particulate filters generally are acid digested for SSMS analysis because of the cohesion and sparking problems that are associated with having glass fibers in the graphite electrodes. It is still preferable, however, to run all particulate samples for SSMS neat, and this will be done whenever possible. Samples for chloride analysis will be prepared by extraction with hot water. When available, these hot water extract solutions will also be the preferred sample for sulfate analysis. Mercury is analyzed by the cold vapor technique, and both arsenic and antimony are determined by hydride generation and AAS detection. The sulfate determination is a turbidimetric procedure, and specific ion electrodes are used to analyze both chloride and fluoride.

In addition to the information generated by the Level 1 procedures, the EPA has additional specific needs for data on the amount of H_2SO_4 (SO_3) emissions on many of the combustion sources that will be studied. For this reason, a series of procedures for the analysis of samples from the controlled condensation system (CCS) for the collection of H_2SO_4 aerosols are included.

8.2 SAMPLE PREPARATION

The following procedures will be used to prepare all Level 1 samples for inorganic analyses. The procedures apply to solid and organic liquid materials since aqueous liquids do not require any preparation. Parr bomb combustion is used to prepare organic solids and liquids (i.e., XAD-2 resin, coal and fuel oil) for SSMS, Hg, SO_4, F, and Cl analyses. Aqua regia digestions are used to dissolve solid samples such as particulates, fly ash, bottom ash, etc. for Hg, SO_4, and F analyses. Whenever possible, SSMS will be performed on neat solid samples. However, particulate catches on glass fiber filters will generally be embedded in the pores of the filter and will require an aqua regia digestion for the SSMS analysis as well. Hot water extractions are used to dissolve Cl in solid samples, since this anion can not be analyzed in aqua regia solutions. Hot water extract solutions are also preferred the SO_4 analysis.

An improved procedure pending EPA approval for extracting inorganic species from XAD-2 resin with acid is given in Section 8.2.3. Reference to this procedure is shown in dotted lines on Figure 8-2.

8.2.1 Parr Bomb Combustion

8.2.1.1 Scope and Application

Parr oxygen combustion is applicable for the preparation of all combustible materials for inorganic analysis. For Level 1 samples, the materials to be combusted are fuel oil, coal, and XAD-2 resin. Significant background quantities of Cr, Fe, Ni, and Mn can be encountered as a result of attack on and leaching of the stainless steel bomb components during combustion. To eliminate this background, samples for SSMS analysis are combusted by a more rigorous method using platinum electrodes and a quartz cup and lid to line the bomb.

8.2.1.2 Apparatus

- Parr oxygen bomb — 342 ml capacity, equipped with platinum electrodes
- Oxygen supply and regulator
- Parr pellet press and die
- Vycor sample cups

- Platinum firing wire
- Glass beakers, 250 ml and 100 ml
- Watch glasses
- Whatman filters, #41
- Nalgene volumetric flasks, 100 ml
- Nalgene funnels
- Quartz cup and lid
- Mortar and pestle, ceramic

8.2.1.3 Reagents

- 4 percent collodion in amyl acetate or equivalent
- 1:1 HNO_3, H_2O
- Benzoic acid

8.2.1.4 Sample Preparation

Three types of samples will be run: fuel oil, coal and XAD-2 resin. No sample preparation is necessary for fuel oil samples; however, the other two sample types will require steps to ensure complete combustion.

- Coal - Weigh 1 g coal into Vycor sample cup, add 0.25 g benzoic acid and mix. Transfer contents to pellet die and press coal sample into pellet.
- XAD-2 Resin - Weigh 1 g of resin into Vycor sample cup. Add ~3 ml of collodion solution, mix and flatten the sample into a cake. Place sample in oven at 110°C for ~20 minutes.

8.2.1.5 Combustion Procedure

- For SSMS Analysis Samples

  Place 1 ml of 1:1 HNO_3 in quartz cup and place in Parr bomb. Place Vycor cup with sample in Pt holder and attach platinum firing wire being certain contact is made with sample. The quartz cup and lid fit the bomb snugly. Care must be taken when placing the quartz lid down onto the cup to assure that the quartz lid forms a seal with the cup. Assemble the bomb and pressurize to 30 atm with O_2. Insert bomb in calorimeter, attach electrical leads and ignite. Allow to cool for ~15 minutes and slowly release the pressure. Disassemble bomb and wash bottom of quartz lid and contents of Vycor cup into quartz cup. Remove the quartz cup and wash the contents into a Nalgene bottle and make up to ~50 ml. Label the sample and turn it in to the Sample Bank Manager.

- For Other Samples (not sensitive to Parr Bomb contamination)

  Place 1 ml of 1:1 HNO_3 in bottom of Parr bomb. Place sample cup in holder and attach platinum firing wire, being certain contact is made with sample. Assemble bomb and pressurize to 30 atm with O_2. Insert bomb in calorimeter, attach electrical leads and ignite.

  Allow to cool for ~15 minutes and slowly relieve pressure. Disassemble bomb and wash contents into 250 ml beaker, cover with a watch glass and digest on hot plate for 30 minutes; do not allow to boil. Cool and filter through a number 41 Whatman filter, supported in a Nalgene funnel, into a 100 ml Nalgene volumetric. Dilute to volume, label, and turn in to Sample Bank Manager.

8.2.2 Aqua Regia Digestion

8.2.2.1 Scope and Application

Aqua regia digestion is used for the preparation of loose particulate, particulate collected on glass fiber filters, and bulk solids (e.g., fly ash and bottom ash) for inorganic analysis. This method is appropriate for species, such as Hg, As, Sb, SO_4, and F, which are soluble in aqua regia.

8.2.2.2 Apparatus

- Distillation flasks, flat-bottom, 200 ml
- Condenser, Liebig or Allihn type
- Hot plate
- Volumetrics, Nalgene, 100 ml
- Filter funnels, Nalgene
- Filter paper, Whatman number 41

8.2.2.3 Reagents

Constant boiling aqua regia — 4 parts conc. HNO_3 + 1 part conc. HCl, mix fresh daily.

8.2.2.4 Procedure

The weighed sample aliquot is placed in the distillation flask. Sixty ml of constant boiling aqua regia solution are added, the condenser attached, and the apparatus secured over a hot plate. The acid is refluxed for ~6 hours at which time the apparatus is removed from the hot plate and allowed to cool. Rinse the contents of the condenser into the distillation flask using 10 ml of deionized water and disconnect the condenser. Filter the contents of the distillation flask through a through a Whatman 41 filter supported by a Nalgene funnel. Collect the filtrate in a Nalgene volumetric and wash the filter with two-10 ml volumes of deionized water. Make the volumetrics to volume, label, and turn the digested samples in to the Sample Bank Manager.

8.2.3 XAD-2 Resin Acid Extraction

8.2.3.1 Scope and Application

The following procecure was developed to replace the Parr Bomb procedure currently used for inorganic analysis of XAD-2 resin. All equipment cleanup procedures, sample disbursement activities, and sample proportioning methodologies are listed. Implementation of this procedure is pending.

8.2.3.2 Apparatus

- Condenser — Pyrex, any type with ₸ 34/45 bottom fitting
- Extraction tube, Soxhlet, Pyrex, top joint ₸ 34/45, bottom joint ₸ 24/40,
- Extraction thimble, Pyrex, with fritted disc, pore size: 40 microns, diameter: 25 mm., height: 85 mm.
- Heating tape — grounded, minimum 6' length
- Asbestos — Cloth tape or sheet minimum 100 square inches
- Jars, amber glass 50 ml., lids with Teflon liners
- Glass wool, Pyrex
- Flask, round bottom, Pyrex, ml. with ₸ 24/40 joint
- Stirring rod, glass diameter: 3/16", length: 10"
- Variac transformer, 117 VAC.

8.2.3.3 Reagents

- Aqua regia — constant boiling — 80% nitric acid plus 20% hydrochloric acid
- Deionized water
- Acetone — reagent grade
- Methylene chloride, Distilled-in-Glass

8.2.3.4 Equipment Cleanup Procedures

Before any activity is undertaken, the following equipment procedure is necessary for all glass apparatus.

1. Wash and soak for 2 hours all glassware in aqua regia.
2. Rinse equipment thoroughly at least six times. Extreme caution and care must be taken to ensure the glass frit in the thimble is thoroughly rinsed.
3. Rinse all equipment once in acetone.
4. Rinse all equipment twice in methylene chloride.
5. Thoroughly dry all equipment.
6. NOTE: Glass wool should also be acid cleaned, solvent rinsed, and dried.

8.2.3.5 Procedure

1. Equipment Setup

   a. Place XAD-2 resin inorganic aliquot in thimble with tightly-packed glass wool on top of the resin in the thimble. This will prevent the resin from floating. Place thimble in the extraction tube.

   b. Place 100 ml. of aqua regia in the round bottom flask.

   c. Assemble the condenser, extraction tube, and flask. Do not use any stopcock grease.

   d. Place assembly on top of a hot plate (if self-standing flask) or use round bottom flask heating mantle. Use appropriate clamps for support.

   e. Carefully wrap the heating tape around the Soxhlet extraction tube section which transmits the heated vapors from the round bottom flask to the condenser. Do not wrap the entire Soxhlet extraction tube assembly with the heating tape.

f. Carefully wrap the entire Soxhlet extraction tube with asbestos tape or cloth. Keep in place with heat resistant tape.

g. Plug the heating tape into the Variac.

2. Extraction Procedure

It is mandatory that the extraction must begin 6 hours before the end of the working day.

a. Turn on the hot plate or heating mantle and adjust the heat until the aqua regia is boiling vigorously.

b. Turn on the heating tape and adjust the heat until aqua regia vapors reach the condenser. At least two turnovers per hour should be achieved.

c. Carefully observe the extraction over the next 6 hours. If the total acid level noticeably drops (33 percent or more), add more aqua regia and check for leaks. Since the Soxhlet will be running overnight, no more than 25 percent of the acid can be lost over a period of 6 hours. There must be at least 25 ml of aqua regia in the round bottom flask at all times.

d. After ensuring all glass joints and seals are properly secured, allow the apparatus to run over night. The entire extraction should run for at least 18 hours.

e. Before disconnecting the system, allow the aqua regia to accumulate in the thimble. Just before the liquid starts to siphon back into the round bottom flask, turn off the heating tape and remove the asbestos cloth. Turn off the hot plate or heating mantle.

f. If the aqua regia siphons into the round bottom flask as the system is cooling, turn on the heat again and allow liquid to accumulate in the thimble. Repeat step (e) above.

g. If there is 30 ml or less of aqua regia remaining in the entire extraction system, turn off all heat and allow the system to cool.

h. After the system cools, save the aqua regia in the round bottom flask for inorganic analyses. Store the aqua regia in an acid cleaned plastic bottle (Nalgene, high density linear polyethylene).

8.2.4 Condensate, XAD-2 Module Wash, XAD-2 Resin Extract, and H_2O_2 Impinger Composite (Pending)

In order to make a single sample from the four discrete samples that may contain inorganic material passing the filter, a proportional composite is made based on the fraction of XAD-2 resin extracted. For example, if 15 percent of the XAD-2 is extracted, 15 percent of each of the other samples is taken and composited with the acid extract samples. Blanks should be determined on the original components and applied to the sample using the appropriate correction factors. In this way, one set of blanks can be used for several sites using the same reagent lots.

8.3 SPARK SOURCE MASS SPECTROGRAPHIC ANALYSIS

8.3.1 Scope and Application

Spark Source Mass Spectrography (SSMS) is used to perform a semi-quantitative elemental survey analysis on all types of Level 1 samples. The procedures described here refer specifically to use of JEOL Analytical Instruments Inc., Model JMS-01BM-2 Mass Spectrograph, but they are also applicable in principle to any other type of spark source instrument. The JMS-01BM-2 is a high resolution, double focusing mass spectrometer with Mattauch-Herzog ion optics and ion sensitive photoplate detection. The instrument is specially designed to carry out high sensitivity trace element analysis of metals, powders, or semiconductor type materials using an RF spark ion source.

8.3.2 Summary of Method

Elemental analysis by SSMS involves the incorporation of a sample aliquot into two conducting electrodes which are decomposed and subsequently analyzed by a mass determination using a double focusing mass spectrometer. Decomposition of the sample electrodes is accomplished by the application of a radio frequency ($\sim$1 MHz) potential of about 4 kV. This induces an electrical discharge in the form of a spark plasma. Because of the high energy associated with the discharge, the spark plasma created is composed primarily of elemental species. The positively charged ions contained in the plasma are accelerated and formed into an ion beam by a high potential electric field ($\sim$30 kV). The beam is then energy focused and momentum dispersed to produce a mass spectrum which is recorded by an ion sensitive photoplate.

Spark Source Mass Spectrography can be used to detect elemental species contained in the sample electrodes at levels down to 10^{-9} grams. Although the sensitivity varies somewhat, depending on the element of interest and the sample type, practically all elements in the periodic table can be detected. Using photoplate detection, all elements having masses in the range 6 to 240 can be detected simultaneously. Concentration data are derived from the intensities (optical density) of the mass spectral lines. There are several methods for determining concentration data from photoplate spectral line densities. The methods vary widely in terms of their complexity and corresponding precision and accuracy of the results. The photoplate interpretation procedures followed for this program and for Level 1 survey work in general are designed to yield concentration data accurate to within a factor of 2 for some 70 elements. A further discussion of precision and accuracy of the technique is given later in this section.

The procedures described here address three major aspects of the analysis: operation of the instrument, electrode preparation, and interpretation of spectral plates. The highlights of each of these activities are described below, with more detail provided in subsequent sections of the manual.

8.3.2.1 Operation of the Instrument

The instrument can be operated conveniently by one person for limited numbers of samples. For analyzing large numbers of samples it is more efficient to use two operators — one to generate the mass spectra and one to analyze the spectral plates. In operating the instrument, the electrode samples are first mounted in the ion source, and the photoplates are mounted in the detection chamber. The system is then evacuated and readied for the generation of mass spectra. Evacuation to typical operating pressures (10^{-8} torr) usually takes 10 to 30 minutes assuming the analyzer and magnetic field sections are maintained in a high vacuum state. The data are acquired by photographing many spectra in successive stages on a single photoplate while the amount of exposure is changed sequentially. A single photoplate can accommodate 16 exposures. The amount of exposure refers to the number of ions deposited on the photoplate in terms of the total ion charge reaching the photoplate. For higher sensitivities, correspondingly longer exposure times are required. For example, 2 to 3 hours (including the pumpdown time) is usually required to detect elements at 1 ppb levels whereas detection at the 3 ppm level usually requires about 1 hour (including the pumpdown time).

The extent of exposure is determined by measuring the total ion charge entering the detection region on a coulomb meter. Typically an exposure range of 10^{-7} to 10^{-13} coulombs is used. Once the spectra have been acquired, the system is vented, and the spectral plates are removed for development and subsequent analysis. The sample electrodes are removed and the ion source prepared for another analysis.

8.3.2.2 Electrode Preparation

In spark source mass spectrometry, conducting materials such as metals are simple pressed or shaped into the desired electrodes. The electrodes are usually cylindrical or rectangularly shaped and are typically 2 x 2 x 15-mm. Nonconducting materials must be ground to a fine powder, mixed with a conducting material (e.g., graphite), and pressed into the desired electrode shape. Electrodes are usually formed with a hydraulic press system. Sample homogeneity is especially important, and care must be taken to ensure the sample and the electrode material are well mixed. In preparing electrodes, there are five major features to be considered:[1] (1) the electrodes must be electrically conducting, (2) the physical strength must be sufficient to tolerate being clamped into the electrode holders, (3) there must be minimum interference from the mass spectrum of the support material, (4) any materials in the support material must be present at low and known concentrations, and (5) for quantitative analysis, the contribution of the support material (and the sample) to the spark and therefore to the total ion current should be constant and consistent. Spectral grade graphite generally meets all of the above requirements as a support matrix for electrode preparation.

8.3.2.3 Plate Reading

In reading the spectral plates, one must first identify the various masses and then establish the relative intensities of the various peaks. Identifying the mass peaks is relatively straightforward; a mass scale is developed using various elements which are known to be present, as well as isotopes and multiply charged ions of these same elements as marker ions. The known elements are introduced into the mass spectrometer in the form of a standard mixture which is sparked under the same conditions as the sample will be run. Once the reference spectrum has been analyzed, a mass scale is developed and marked at convenient mass intervals, usually 5 to 10 atomic mass units. The unknown spectrum is then compared with the reference sample in order to identify the components present.

Establishing the intensities of the various lines is less straightforward. Quantitative intensity data are best obtained with microdensitometers which measure photographic darkening in terms of percent transmittance. Transmittance data are then converted to units of intensity or ion density, which are proportional to the number of ions that cause the darkening. This conversion can be performed in a number of ways: manually, using digital or analog computers[3-9]; with experimental calibration data[2, 10, 11]; or with theoretical relationships,[12] which include some experimentally determined parameters. All of the above techniques suffer to a large degree from at least one of the following: inflexibility, imprecision, insufficient allowance for corrections, large time requirements, and high cost. The simplest method for evaluating spectra is done manually and is usually referred to as the disappearing line technique. Here, the aim is to determine the ratio of the minimum exposures (in coulombs) at which the low level impurity element and a major element in the electrode matrix or an internal standard (spike) are just detectable on the photoplate. To perform the analysis, a series of spectra are taken using the total beam monitor to control the exposure. After the series of spectra are recorded, the exposures at which the impurity line and matrix line "disappear" are determined visually by examining the spectra under magnification (or magnified projection). The exposure ratio thus determined may then be used to obtain concentration data as described in detail later in this section.

8.3.3 The Apparatus

The JMS-01BM-2 is a high resolution, double focusing mass spectrometer with Mattauch-Herzog ion optics. The instrument is specially designed to carry out high sensitivity trace element analysis of metals, semiconductors and miscellaneous powders with the aid of an RF spark ion source and photoplate detection. The instrument may also be fitted with an electrical detection system which can be used as desired. The instrument has a resolution ($M/\Delta M$) of 10,000 using photoplate detection and can detect elements as low as 10^{-9} atomic fraction. All elements are detected simultaneously with a single exposure covering a mass range of mass ratio 1:36 (e.g., Li to U in a single exposure). The instrument maintains a very high vacuum; typically, pressures on the order of 10^{-8} torr are necessary for adequate performance. Brief descriptions of the major components and the operating parameters used for this program are given below.

- Ion Source — An RF spark ion source is used. The sample (in the form of rod electrodes) is placed in a pair of sample holders. A radio frequency high voltage is then applied to the sample.

  The ion source parameters used for all analyses are as follows:

  — RF pulse oscillator:

  Oscillating frequency: approx. 1 MHz

  Anode potential: approx. 4 kV

  Pulse width: 20 or 40 μsec

  Pulse repetition frequency: 300 or 100 Hz

  — Accelerating voltage power supply unit:

  Accelerating Voltage: approx. 27.8 kV

  The source is fitted with a cryosorption pumping attachment that absorbs residual gases in the source region which increases the vacuum and reduces background spectra. It is also equipped with a sample cooling unit which can be used to maintain a sample temperature of 77°K (using liquid nitrogen). This permits the effective analysis of low melting point materials, as well as further increasing the degree of vacuum.

- Automatic Spark Gap Controller — The JMS-01BM-2 is equipped with an automatic spark gap controller which considerably enhances the reproducibility of the analysis. This unit continuously monitors the electrode gap potential and, via a servo-mechanism, maintains a constant spark gap and uniform sparking conditions. For the present program, all analyses are carried out with an electrode gap of 180 μm.

- Monitors — The ion beam current is monitored by an ammeter with full-scale outputs in the range 1 μ-amp to 30 pico-amps selectable in twelve increments. The total ion charge reaching the photoplate is monitored by a vibrating reed electrometer and is used to control the photoplate exposure. The electrometer can automatically control total ion exposures in the range 1000 μ-coulombs to 1 pico-coulomb.

- **Detector** — The JMS-01BM-2 can be equipped with either electrical or ion sensitive photoplates detection. For this program, the Ilford Q_2 (15 x 2 x 0.040 inch) ion sensitive photoplate is used for spectral data collection.

- **Synchronous Passer** — A Synchronous Passer is placed between the ion source and the electrostatic analyzer to control the ion beam so that mass spectra with differing exposures (from long to short exposure times) are photographed under constant sparking conditions. The pulse applied to the deflection gate is synchronized with the spark pulse from the ion source, thus improving the accuracy of quantitative determinations. The specifications of the synchronous passer are as follows:

  Pulse width: 60 μsec

  Pulse repetition frequency: 1, 3, 10, 30, 100, 300, 1k, 3k, 10 kHz

  Voltage: DC 400V

- **Electrostatic Field Unit** — A spherical lens with the following specifications is incorporated to improve the ion current density and sensitivity:

  Rotation angle (ϕ_e): 30°

  Mean radius (r_e): 200 mm

  Voltage: approx. 2.8 kV

  Stability: 40 ppm/40 min

- **Magnetic Field Unit** — The magnetic field unit parameters are listed below:

  Rotation angle (ϕ_m): 90°

  Mean radius (r_m)

  Photoplate detection: max 315 mm
min 52 mm

  Field current supply: 4.0 amps (approx. 7,500 gauss)

  Field current stability: 2×10^{-5} amps/40 min

- Vacuum System — The vacuum system is comprised of the following elements:

Rotary Pumps:	150 ℓ/min 80 ℓ/min
Oil diffusion pumps:	6 inches
(with liquid nitrogen cold traps)	4 inches 2.5 inches
Ion getter pump:	160 ℓ/sec

The ultimate degrees of vacuum (and the vacuum required for sample analysis) for the system components are:

Ion Source:	2×10^{-8} (5×10^{-7}) torr
Electrostatic Field:	5×10^{-9} (3×10^{-8}) torr
Magnetic Field:	1×10^{-8} (1×10^{-7}) torr

8.3.4 Reagents

- Graphite - High purity, spectrographic grade graphite is needed for preparation of electrodes, e.g., ultrasuperior purity graphite powder, Ultra-1-N-USP, from Ultracarbon Corp., Bay City, Michigan or National Spectrographic Grade SP-1 from Union Carbide Corp., New York, N.Y.

- Spex Mix Standard Mixtures - For routine calibrations, standard mixtures of elements are required. These are conveniently provided in: Spex Mix - a mixture of 40 elements as salts or oxides in which each element is present at 1.27 percent by weight; Spex Rare Earth Mix - a mixture of 16 rare earth elements at concentrations of 5.28 percent each; Spex Noble Metal Mix - a mixture of 10 noble metals at concentrations of 9.32 percent each (Spex Industries, Inc., Metuchen, New Jersey). Individual elements in a variety of compound forms at very high purity (4-9's to 6-9's) may also be obtained from Spex Industries.

- National Bureau of Standards, Standard Reference Material - As primary standards, the following NBS standard reference materials (SRM) are required: SRM 1632 trace elements in coal, SRM 1633 trace elements in coal fly ash, and SRM 1634 trace elements in oil.

- Internal Standard - All samples analyzed will be "spiked" with indium. The internal standard will be added as a solution prepared from high purity $InNO_3$, deionized-distilled water, and Ultrex HNO_3 as required.

- Photoplates - Ilford Q2 ion sensitive photoplates are used for obtaining spectra.

- Developer - Ilford ID-13 developer is used for developing plates.
- Ethanol - High Purity (Gold Seal) ethanol is used as wetting agent to facilitate electrode preparation.

8.3.5 Procedures

The individual procedures to be followed in performing SSMS analysis are described below. In general, the details of instrument operation have been omitted; the manufacture's instruction manual should be consulted for these details. Quality Control functions peculiar to the SSMS analysis are indicated where appropriate.

8.3.5.1 Electrode Preparation

Sample aliquots for SSMS electrode preparation are obtained from the Sample Bank either as prepared liquids or as neat solids.

Solid samples must be of a particle size fine enough to pass through a 100-mesh sieve (a powder the consistency of flour). If solid samples of large particle size are received, they must be ground with an agate mortar and pestle before an aliquot is removed for electrode preparation. The optimum aliquot size for solid samples is 50-150 mg. While somewhat smaller samples can be effectively analyzed, samples sizes of less than 10 mg should not be used.

For liquid samples, the volume used for electrode preparation should be that which produces the desired detection limits. As for solid samples, the resulting solids content of the electrode set should not exceed 150-200 mg. Preparing electrodes with the desired properties from liquid samples may be predicted from knowledge of the sample type and/or determined by trial and error, Generally, when preparing impinger-composite or water samples, 20 ml of solution is sufficient. For extract and Parr-bombed aliquots, the initial amount of sample prepared should be taken into consideration prior to electrode preparation.

The steps necessary for adequate electrode preparation for both solid and liquid samples are detailed below.

- Solid Samples

  1) Accurately weigh the sample aliquot and transfer to a Vycor evaporating dish.

2) Wet the sample aliquot with about 1 ml of DDI water, add the appropriate amount of graphite (the graphite added should yield a total solids weight of approximately 250 mg which is sufficient to prepare a set of 3 electrodes), the internal standard (usually ∿10 μg of In), and 3 drops of Gold Seal Ethanol.

3) Slurry the electrode mixture with a Nylon rod, place under an IR lamp, and heat to near dryness. Before the mixture is completely dry, extinguish the lamp and allow to cool. (The remaining liquid will evaporate from the heat of the dish.) Repeat the slurrying process with 1 ml of water and 3 drops of ethanol at least 3 times.

4) Transfer the electrode mixture to an agate mixing vial and further homogenize the sample by mixing in a mixer mill (Spex Industries) for 30 minutes.

5) Pack the electrode mixture into a polyethylene electrode slug with a Teflon funnel and Nylon rod. Place the slug in a suitable metal die, and apply 12 tons/in^2 of pressure for 30 seconds.

6) Allow the die to stand for 15 minutes and remove the slug. The electrodes may be stored in the slug until analysis.

- Liquid Samples

1) Pipette the appropriate volume of liquid into a Vycor evaporating dish and pre-concentrate to a few ml under an IR lamp. Wash down the sides of the dish with about 2 ml of DDI water.

2) Spike the concentrate with the internal standard (as above), add an appropriate amount of graphite, and 3 drops of ethanol.

3) Continue the electrode preparation from step a.3 above.

8.3.5.2 Spectral Data Collection

Prior to data collection, the instrument should be prepared for analysis (consult the Manufacturer's Instruction Manual as necessary) by setting the instrumental parameters and evacuating the various system components to the values specified in Section 8.3.3. In addition, the ion sensitive photoplates should be pre-evacuated under diffusion pumping for at least 6 hours before being placed in the detection chamber. They should be allowed to condition for at least 30 minutes in the detection chamber before spectra are accumulated. The following list enumerates the discrete operations associated with spectral data collection.

1) Secure the sample electrodes in the tantulum holders so that about 5 mm of the electrodes protrude, and mount on the source flange (the electrodes should be handled with clean stainless steel forceps, and care should be taken to prevent contamination from overhandling). Adjust the electrodes in the X-, Y-, and Z- directions for a horizontal electrode — gap to accelerating slit distance of 5-6 mm. Restore the source flange in its housing and evacuate to $\sim 10^{-7}$ torr.

2) Apply the anode potential and accelerating voltages and spark the electrodes. If transmission is not up to specification, refer to alignment procedures.

3) Pre-spark the electrodes in order to remove any loose particles and possible surface contamination. The pre-sparking period should be sufficient to collect about 50 nC of charge. After loose particles are removed and the electrodes are out-gased, a source pressure less than 5×10^{-7} should be obtainable. If proper source vacuum is not achieved, activate the source and sample cryopumping units as necessary.

4) Adjust the inter-electrode distance (gap) while monitoring the automatic spark gap controller. First, short the electrodes and zero the controller. Second, separate the electrodes (cease sparking) and adjust the controller gain to 15 volts. Finally, close the gap until the gap voltage drop is 7.5 volts; for graphite electrodes this corresponds to a gap width of 180 μm. Place the controller unit in automatic operation for the duration of the data collection phase. If subsequent tuning of the instrument becomes necessary, repeat the above steps and establish stable sparking conditions before collecting spectral data.

5) Obtain a graded series of exposures on the photoplate by collecting spectra with the total charge accumulations and beam control conditions given in Table 8.1. The ion beam control parameters given in Table 8.1 are typical and serve as a guide to proper spectral data collection. In general, the ion current passed to the photoplate should not exceed 1×10^{-9} amps. Ion currents exceeding this value tend to increase the system vacuum and therefore ion collisions (produce charge exchange spectra) and increase secondary ion images in the form of excessive photoplate fogging. In this event, implement synchronous passing and beam chopping as appropriate to limit the ion current. In general, the beam chopping should be scaled according to the scheme shown in Table 8.1.

6) Remove the exposed photoplate from the detection chamber and the analyzed electrodes from the source, and ready the instrument for subsequent analyses.

7) Develop exposed photoplates using Ilford ID-13 developer prepared at one half the recommended strength for 5 minutes (twice the recommended development time.[13] Stop the plate development in standard photographic stop-bath for 15 seconds, and fix the plate for 3 minutes in standard photographic fix solution with hardener. Wash the developed plates for 30 minutes in running water.

Table 8.1. Suggested Instrument Conditions for Obtaining Mass Spectral Data as a Graded Series of Exposures.

Photoplate Level	Stage	Relative exposure	Coulomb exposure	Beam* chopping frequency (Hz)	Count	Coulomb meter full scale	Synchronous passer
0	0	Prespark	5×10^{-8}	-	50	1×10^{-9}	Pass
2	1	12,000	1.2×10^{-7}	-	120	↓	↓
4	2	6,000	6×10^{-8}	-	60	↓	↓
6	3	3,000	3×10^{-8}	-	30	↓	↓
8	4	1,500	1.5×10^{-8}	-	15	↓	↓
10	5	800	8×10^{-9}	-	8	↓	↓
12	6	400	4×10^{-9}	-	4	↓	↓
14	7	200	2×10^{-9}	-	2	↓	↓
16	8	100	1×10^{-9}	-	1	↓	↓
18	9	50	5×10^{-10}	100	1	3×10^{-10}	Chop
				30	2	1×10^{-10}	↓
20	10	25	2.5×10^{-10}	30	2	1×10^{-10}	↓
				10	1	3×10^{-11}	↓
				3	2	1×10^{-11}	↓
22	11	12	1.2×10^{-10}	30	1	1×10^{-10}	↓
				3	2	1×10^{-11}	↓
24	12	6	6×10^{-11}	10	2	3×10^{-11}	↓
26	13	3	3×10^{-11}	10	1	3×10^{-11}	↓
28	14	1.5	1.5×10^{-11}	10	0.5	3×10^{-11}	↓
30	15	0.75	7.5×10^{-12}	1	1.5	3×10^{-12}	↓
32	16	0.40	4.0×10^{-12}	1	1	3×10^{-12}	↓
				1	1	1×10^{-12}*	↓

*These settings are typical for a spark repetition rate of 300 Hz and a resulting ion current less than 1 nC. Depending on the ion current and charge accumulation rate, it may be necessary to reduce the beam chopping frequency and spark repetition rate.

8.3.5.3 Photoplate Interpretation

The interpretation of spectral data collected on a photoplate consists of two discrete operations. The first, and obviously the most critical, is the qualitative interpretation; i.e., the assignment of a mass spectral line to a particular element. The second involves a determination of the relative number of ions which produced the spectral line (the relative concentration of the element). The steps to be carried out in order to make these determinations are given below.

1) Develop the mass/charge (m/e) scale using the $^{12}C_n$ (e=1) spectral lines and the spectral lines of elements known to be present (multiple isotopes and multiply charged ions are also useful). Mark the photoplate according to the nominal mass scale so developed. A numbering every 5-10 mass units is sufficient.

2) Determine the probable presence or absence of each element of interest. For an unambiguous determination, at least one of the following criteria (in order in decreasing importance) must be met:

   a. The isotopic abundance ratios agree with the naturally occuring fractional abundances.

   b. Multiply charged ions (e = 2,3,. . .) of the element of interest can be identified.

   c. A mass measurement of sufficient accuracy to confirm the presence of the element in question can be made.

3) Confirm the presence of each element deemed probable in Step 2 by ruling out all interferences likely to be present. Possible interferences are dimers, trimers, oxides, and carbides of elements present in high concentrations and hydrocarbon molecules. Hydrocarbon molecules are easily recognized since they form "runs" consisting of C_nH_{n+x} (where x = 1,2,3,...), and the distribution of intensity about x = 2 is symmetrical. Hydrocarbon runs occur only in samples of high organic content. If these interferences are too severe for effective photoplate interpretation, the sample should be combusted according to Section 8.2 and reanalyzed.

   If photoplate interpretation is straightforward, all elements whose presence can not be ruled out nor confirmed should be quantified according to the methods described below and identified with "less than" values.

4) Determine the relative exposures of the spectral line of each element of interest which is "just detectable" as a line on the photoplate. For spectral lines which are more than "just detectable" on a given stage but are completely absent on the following stage, a logarithmic interpolation of the exposure should be made (the interpolation is logarithmic owing to the characteristic response of ion sensitive photoplates).

5) For all spectral lines for which a "just detectable" exposure can not be determined, measure the percent transmittance (percent T) of one or more exposure levels. The lines chosen for percent T measurement should be free from line-broadening, i.e., fall within the limits of the typical linewidth versus mass characteristic curve (see below), and have optical densities in the range 0.2 to 0.5; i.e., percent T's in the range 63 to 30 percent. Elements which have no spectral lines which met the above criterion are denoted as major components (MC) of the sample. It should be noted that MC concentrations can indicate actual concentrations in the range 0.5 to 100 percent depending on the particular element under analysis.

6) Determine the "just detectable" exposure of the internal standard. If percent T measurements were required for elements of interest, measure the percent T of all standard lines which meet the above criteria.

8.3.5.4 Calibration Parameters

As with all analytical methods, a SSMS analysis relies on a calibration via the determination of several instrumental parameters. These determinations need not be made prior to each sample analysis but as an initial calibration procedure and should be repeated on a periodic basis as part of the quality assurance program. The principal calibration requirements, and the suggested frequency of determination are given below.

1) The mass resolution should be known prior to interpretation of spectral data. While the resolution is of prime importance to the qualitative determination of the presence of an element, it is the ultimate consideration in ruling out an interfering species. Hence the instrumental resolution can both confirm elemental composition and lend credit to the quantitative determination. The resolution is primarily a function of the main slit (first slit at ground potential) width. Theoretically, the resolving power is given by $R_0 = r_e/S_0$, where r_e is the rotation radius of the electrostatic field, and S_0 is the main slit width. In practice, the resolution is measured according to $R = \overline{M}/\Delta M$, where $\overline{M}$ is the mean mass of the M/e lines of interest, and ΔM is the mass separation. For typical environmental samples, a resolution of greater than 3,000 is desirable.

2) The photoplate response to an ion is primarily a function of its mass and energy (for emulsion based photoplates). For constant charge(e), the response of Ilford Q2 photoplates varies approximately as $m^{-1/2}$; e.g., Li is the most sensitive and U the least. Also, the greater the charge (the more energetic), the greater the response. The $m^{-1/2}$ variation in response of the Ilford Q2 photoplate is well documented in the literature and can be verified most easily by recording the response produced by elemental species with multiple isotopes (Li and W are suitable choices).

3) The spectral line width is primarily a function of ion-optics employed in the spectrometer; i.e., a function of the ion beam focusing. An instrument with Mattauch-Herzog ion optics in "perfect" focus should yield a spectral line whose relative width is proportional to the square root of the mass, M. In practice, mass spectrometers are not capable of perfect focus, and in many cases it is desirable to use other focal arrangements. Therefore, the spectral line widths should be determined experimentally for each focal setting and after any change in focal setting.

4) The relative sensitivity of the SSMS analysis to a particular elemental species depends on a number of factors including ionization potentials, bond or dissociation energies, boiling points, heats of sublimation, etc., as well as instrumental parameters. Since many of these variables are compound-specific, the use of well characterized standards whose matrices closely resemble sample matrices is highly desirable.

For the present program, sample types analyzed by SSMS can be grouped into two basic categories: 1) particulate or fly ash, and 2) extracts or solutions which contain excess nitric acid. Therefore, the sensitivity factors used for this program are determined from 1) NBS SRM 1633 Fly Ash Standard, and 2) a laboratory prepared standard containing the nitrate salts (or nitric acid dissolution of the oxides) of all elements of interest. Sensitivity factors are determined relative to an indium value of unity in all cases.

In general, the relative sensitivity factors (RSFs) are determined by running the standard materials under experimental conditions identical to the conditions used when running samples. Calculations of RSF data using the "just detectable" line technique for exposure measurements should be carried out using a minimum of six determinations so that statistically meaningful data result.

8.3.6 Calculations

As indicated in the above procedures, the elemental concentration data are obtained by the "just detectable" line technique when possible and from percent T data, otherwise. In either case, variables to be determined are the exposures necessary to produce identical responses for the unknown and internal standard mass spectral lines. Concentration data may then be calculated according to

$$C_u = C_k \cdot E_R \cdot A_R \cdot W_R \cdot M_R/S_R$$

where C_u — is the unknown concentration;

C_k — is the known concentration (internal standard);

E_R — is the ratio of the exposure (E_k/E_u) required to yield the same spectral intensities for both the known and unknown elements;

A_R — is the ratio (A_k/A_u) of the fractional abundance of the isotopes used for the determination;

W_R — is the ratio (W_u/W_k) of the relative widths of the spectral lines;

M_R — is the ratio (M_u/M_k) of the photoplate response to the known and unknown isotope masses;

S_R — is the instrumental sensitivity of the unknown relative to the known.

Clearly, when using the "just detectable" line technique for exposure determinations, the variables W_R, M_R, and S_R can be combined to yield a single instrumental sensitivity factor. However, this is not the preferred method when percent T data are being used. In addition, the separation of the instrumental parameters from the elemental sensitivities serves a quality control function in that many useful trends (with respect to atomic group and period) are present in the S_R data which are useful in troubleshooting problems.

8.3.6.1 Treatment of Standards

Standard mixtures are used for the determination of the relative sensitivity factors and for routine quality control checks. The standard mixtures should be analyzed under conditions identical to those used for sample analysis. In addition, the standard material matrix should match, as closely as possible, the sample matrix. This will allow for the determination of reliable elemental sensitivity data and possible interferences.

Photoplate data for the standard materials are collected and interpreted according to the procedures described above. Mass responses, M_R, should be verified and spectral line widths measured according to 8.3.5. Relative sensitivity data can be determined by rearranging the concentration equation given above and calculating S_R for each element using the known standard concentrations.

8.3.7 Precision and Accuracy

Spark Source Mass Spectrometry in general is a semiquantitative tool. Although precisions of ±5 to 10 percent can be achieved,[14] the methodology for such analyses are very time-consuming when comprehensive elemental surveys are being performed. Typical factors which affect the precision and accuracy of SSMS analyses include sample homogeneity, preparation of electrodes which adequately represent the sample, photoplate irregularities, spark discharge characteristics, and the general lack of well-characterized standards. In addition, the methods used for spectral line intensity determinations can limit the precision and accuracy *a priori*. The methodology employed for the present program was designed to yield precision on the order of 50 to 100 percent. While absolute accuracies depend on the quality of the standards used, typical accuracies of 100 to 200 percent are obtained.

8.3.8 References

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8.4 MERCURY ANALYSIS

8.4.1 Scope and Application

The cold vapor mercury analysis described here is applicable for the Level 1 and Level 2 determination of Hg in hydrogen peroxide and ammonium persulfate impinger solutions, bulk liquids, dilute HNO_3 solutions resulting from the Parr Bomb combustion of fuels and XAD-2 resin samples, and aqua regia solutions from the digestion of particulates. Sensitivity and detection limits are 0.004 and 0.001 μg, respectively, with an upper limit of 0.25 μg.

8.4.2 Summary of Method

The cold vapor mercury analysis is based on the reduction of mercury species in acid solution with stannous chloride and the subsequent sparging of elemental mercury, with nitrogen, through a quartz cell where its absorption at 253.7 nm is monitored.

8.4.3 Apparatus

- Mercury reduction apparatus. The usual design, consisting of a jar incorporating a two-hole rubber stopper through which a gas bubbler tube and a short gas outlet tube pass, can be used. The TRW design is essentially a U tube with a glass frit on one side. The frit serves as a mixing device as well as the gas bubbler, thus eliminating the need for a separate magnetic stirrer and a stirring bar to mix the reductor contents.

- Atomic absorption spectrophotometer. Use a mercury hollow cathode lamp at a wavelength of 253.7 nm. (or equivalent)

- Absorption cell. A cylindrical tube approximately 25 mm I.D. x 125 mm long, with quartz windows, and incorporating inlet and outlet side arms to permit introduction and discharge of carrier gas. This type of cell is available commercially from several manufacturers of atomic absorption equipment, or it may be constructed from readily available materials. In the latter case, the cell should be tested carefully for possible leakage after assembly. The cell is mounted in the optical path of the AAS.

- Flowmeter. Capable of measuring a gas flow on the order of 1.9 liters/min (4 ft^3/hr).

- Scavenging tube. This tube is filled with soda lime and is connected between the gas outlet tube of the reduction vessel and the inlet side arm of the absorption cell with Tygon tubing. The soda lime is replaced every 25 determinations; otherwise, a loss in sensitivity occurs.
- Erlenmeyer flasks, 125 ml
- Beakers, 150 ml
- Pellet press
- Funnels
- Filter paper, Whatman #41

8.4.4 Reagents

- Stock Mercury solution, approximately 1 gram/liter (1000 ppm). Weigh one gram of pure, elemental mercury to the nearest 0.1 mg and dissolve in a solution consisting of 150 ml deionized water and 50 ml concentrated HNO_3 (sp. gr. of 1.42). Dilute this solution to 1000 ml with deionized water. The final solution contains approximately 1000 ppm mercury (record exact concentration) in a matrix of 5 percent (v/v) nitric acid. A commercially obtained 1000 ppm Hg solution can also be used.
- Standard mercury solutions. Prepare working standard solutions of mercury down to 1 ppm by serial dilutions of the 1000 ppm Hg stock solution with 5 percent (v/v) HNO_3. Such solutions can be assumed to be stable for up to one week. Below 1 ppm Hg, standard solutions should be prepared daily and diluted with 5 percent (v/v) HNO_3 and/or deionized water as appropriate so the final solution matrix is approximate 1 percent (v/v) HNO_3.
- 1:1 Nitric acid solution. Dilute 500 ml conc. nitric acid to 1000 ml.
- Stannous chloride solution. Dissolve 20 g of $SnCl_2.H_2O$ in 20 ml conc. HCl (warm the solution to accelerate the dissolution process) and dilute to 100 ml.
- Potassium permanganate solution. Dissolve 5.0 g $KMnO_4$ in deionized water and dilute to 1 liter.
- Nitrogen carrier gas.
- Nitric acid, conc.
- Hydrochloric acid, conc.
- Benzoic acid.

8.4.5 Procedure

8.4.5.1 Standardization

Standards in the range of 1-10 ppb are made. To the reduction vessel, transfer 10 ml 1:1 nitric acid solution, 3 ml conc. H_2SO_4, 5 ml of a standard solution, and deionized water to bring the volume to a total of 50 ml. Add 5 ml of stannous chloride solution. Close the system and immediately initiate the nitrogen flow. The optimum flow rate will vary from system to system, therefore, several flow rates should be tried until maximum sensitivity is obtained. Repeat the procedure for varying concentrations of mercury throughout the specified range. The glass frit is cleansed in between analyses by flushing with 1:1 nitric acid followed by deionized water. Blanks should be run using deionized water. Plot absorption (peak height) against standard concentration to obtain a calibration curve.

8.4.5.2 Analysis

In the determination of mercury by the cold vapor technique, certain volatile organic materials may absorb at 253.7 nm. If this is expected, the sample should be analyzed by the regular procedure and again under oxidizing conditions, i.e., without the addition of stannous chloride. The true mercury concentration can be obtained by taking the difference of the two values.

- Aqueous samples are analyzed by the same procedure as that used for standardization. If a larger sample size is used resulting in a total volume greater than 50 ml, a new calibration curve must be constructed using the new total volume.
- 3M H_2O_2 has shown an interference by consuming the stannous chloride reducing agent. This problem is circumvented by decomposing the excess H_2O_2 with permanganate prior to stannous chloride addition. Pipet an aliquot into a 125 ml Erlymeyer and add 10 ml conc. HNO_3. Add $KMnO_4$ solution with stirring until the MnO_2 precipitate that forms will not redissolve. At this point add 2 ml conc. H_2SO_4 and 1 drop 30 percent H_2O_2. After precipitate has redissolved continue adding $KMnO_4$ dropwise until a permanant reddish color is obtained. Transfer contents to reduction apparatus and adjust volume to approximately 50 ml. Proceed as per the standardization procedure.

- The presence of the silver nitrate catalyst in the ammonium persulfate solution has been shown to yield low Hg recoveries. Removal of Ag^+ by addition of Cl^- followed by filtration has been found to be an effective procedure for the removal of this interference. Pipet an aliquot into a 150 ml beaker. Add 10 ml conc. HNO_3 and 2 ml HCl. Filter through #41 Whatman filter. Wash several times with deionized water and dilute filtrate to approximately 50 ml. Transfer filtrate to reduction vessel and proceed as per standardization procedure.

- In analyzing organic solids, aliquots from Parr bomb decomposition over acid are used. If there is doubt as to whether the sample has undergone complete oxidation during combustion, add 5 percent potassium permanganate solution dropwise until a pink color persists. Proceed with the determination as described under standardization. As the bomb ages, there may be a tendency for mercury to become trapped in the bomb wall fissures during combustion. In addition, if the same bomb is used for normal calorimetry work, there may be a tendency for mercury to accumulate in the bomb with time. Consequently, before a series of mercury determinations is undertaken, several blank determinations should be made by firing benzoic acid pellets (approximately 1 gram) in place of the sample. Benzoic acid firings should be repeated until a stable, consistently low blank value is obtained. This final blank value is then used to correct the mercury values obtained for subsequent samples. The condition of the interior of the bomb should be inspected at frequent intervals. If evidence of significant pitting or corrosion is observed (usually indicated by erratic mercury values for samples or benzoic acid blanks), the bomb should be returned to the manufacturer for reconditioning.

- To analyze particulates, aliquots from the aqua regia digestion are used. Proceed with the determination as described under standardization.

8.4.6 Calculation

Compare the absorption of the samples to the calibration curve and calculate the amount of mercury content as follows:

$$\text{Hg content (ppm)} = \frac{W}{V}$$

Where

W = weight of mercury, μg

V = volume of aliquot, ml

8.4.7 Precision and Accuracy

Mercury at a concentration of 0.4 μg/liter yields a precision of ±21.2 percent RSD with a relative error of 2.4 percent.

8.5 ARSENIC ANALYSIS

8.5.1 Scope and Application

Arsenic analysis by hydride generation and atomic absorption spectrometric detection is applicable for Level 1 analysis of impinger solutions, coal, fly ash and XAD-2 resin samples. Detection limit for the procedure is 0.1 μg with a calculated sensitivity of 0.8 μg. Either of two arsine evolution methods can be used: gas can be generated in a reaction with stannous chloride and zinc slurry, or in a reaction with sodium borohydride. Some interferences have been reported for this arsenic procedure. In particular, it has been found that excess H_2O_2 and HNO_3 must be removed prior to the addition of either the Zn slurry or $NaBH_4$.

8.5.2 Summary of Method

The procedure entails the reduction and conversion of arsenic to its hydride in acid solution with either $SnCl_2$ and metallic Zn or $NaBH_4$. The volatile hydride is swept from the reaction vessel, in a stream of argon, into an argon-hydrogen flame in an atomic absorption spectrophotometer. There, the hydride is decomposed and its concentration monitored at the resonance wavelength 193.7 nm. Arsenic reaction stoichiometry is 1:1.

8.5.3 Apparatus

- Flow meter, capable of measuring 1 liter of gas/min.
- Medicine dropper, capable of delivering 1.5 ml, fitted into a size "0" rubber stopper.
- Reaction flask, 50 ml capacity pear-shaped vessel with side arm having $ 14/20 joints on both the neck and side arm.
- Special gas inlet-outlet tube, constructed from a micro cold finger condenser by cutting off the portion below the $ 14/20 ground glass joint.
- Magnetic stirrer, strong enough to homogenize the zinc slurry.
- Drying tube, 10-cm long polyethylene tube filled with glass wool to keep particulate matter out of the burner.

- Apparatus setup involves: 1) connecting the outlet of the reaction vessel to the auxiliary oxidant input of the spectrophotometer burner with Tygon tubing and 2) connecting the inlet of the reaction vessel to the outlet side of the auxiliary oxidant (argon supply) control valve of the instrument.

8.5.4 Reagents

- Potassium iodide solution: Dissolve 20 g KI in 100 ml deionized water.

- Stannous chloride solution: Dissolve 100 g $SnCl_2$ in 100 ml conc. HCl.

- Zinc slurry: Add 50 g zinc metal dust (200 mesh) to 100 ml deionized water.

- Diluent: Add 100 ml 18 N H_2SO_4 and 400 ml conc. HCl to 400 ml deionized water in a 1 liter volumetric flask and bring to volume with deionized water.

- Sodium borohydride solution: Dissolve 5 g $NaBH_4 \cdot H_2O$ in 100 ml deionized water. Make fresh prior to each use.

- Arsenic solutions:

  1) Stock arsenic solution: Dissolve 1.3209 g arsenic trioxide, As_2O_3, in 100 ml deionized water containing 4 g NaOH and dilute to 1000 ml with deionized water. 1.00 ml solution contains 1.00 mg As.

  2) Intermediate arsenic solution: Pipet 1 ml stock arsenic solution into a 100 ml volumetric flask and bring to volume with deionized water containing 1.5 ml conc. HNO_3/liter. 1.00 ml solution contains 10 μg As.

  3) Standard arsenic solution: Pipet 10 ml intermediate arsenic solution into a 100 ml volumetric flask and bring to volume with deionized water containing 1.5 ml conc. HNO_3/liter. 1.00 ml solution contains 1 μg As.

8.5.5 Procedures

8.5.5.1 Instrument Operation

Because of differences between makes and models of satisfactory atomic absorption spectrophotometers, it is not possible to formulate instructions applicable to every instrument. In general, proceed as follows:

1) Install an arsenic hollow cathode lamp in the instrument, and align the lamp in accordance with the manufacturer's instructions.

2) Set the wavelength selector at 193.7 nm.

3) Set the slit width according to the manufacturer's suggested instructions for analyzing As.

4) Turn on the instrument and apply the amount of current to the hollow cathode lamp suggested by the manufacturer.

5) Allow the instrument to warm up until the energy source stabilizes. This process usually requires 10 to 20 min.

6) Install a Boling burner head.

7) Turn on the argon and adjust to a flow rate of about 8 liters/min, with the auxiliary argon flow at 1 liter/min.

8) Turn on the hydrogen, adjust to a flow rate of about 7 liters/min and ignite the flame. The flame is essentially colorless. To determine whether the flame is ingited, pass the hand about 30 cm (1 ft) above the burner to detect the heat emitted.

9) Atomize the standard solution (1.00 ml = 1.00 µg of arsenic) and adjust the burner both sideways and vertically in the light path until maximum response is obtained.

10) The instrument is now ready to run standards and samples.

8.5.5.2 Sample Preparation

a) Condensate sample - Add 25 ml sample, 20 ml conc. HCl and 5 ml 18 N H_2SO_4 to a 50 ml volumetric flask.

b) Peroxide samples, aqua regia and nitric acid solutions - To a 25 ml aliquot in a 150 ml beaker, add 5 ml conc. HNO_3 and 6 ml 18 N H_2SO_4. Evaporate to SO_3 fumes. To avoid the loss of arsenic, maintain oxidizing conditions at all times by adding small amounts of nitric acid whenever the red brown NO_2 fumes disappear. Cool, transfer to a 50 ml volumetric, add 20 ml conc. HCl, and dilute to volume.

c) Ammonium persulfate samples - Add 5 ml conc. HNO_3 and treat as in b).

d) Coal and XAD-2 resin samples - Treat Parr bomb solutions as in b).

8.5.5.3 Preparation of Standards

Transfer 0.5, 1.0, 1.5, and 2.0 ml of standard arsenic solution to 100 ml volumetric flasks and bring to volume with diluent to obtain concentrations of 5, 10, 15, and 20 µg/liter arsenic.

8.5.5.4 Treatment of Samples and Standards

Transfer a 25 ml portion of sample prepared as in Section 8.5.5.2 or standard prepared as in Section 8.5.5.3 to the reaction vessel and add 1 ml potassium iodide solution to arsenic samples and standards. If the Zn slurry addition method is to be followed, add 0.5 ml $SnCl_2$ solution. Allow at least 10 minutes for the metal to be reduced to its lowest oxidation state. Attach the reaction vessel to the special gas inlet-outlet glassware. Fill the medicine dropper either with 1.50 ml zinc slurry that has been kept in suspension with the magnetic stirrer, or with 1.50 ml $NaBH_4$ solution. Firmly insert the stopper containing the medicine dropper into the side neck of the reaction vessel. Squeeze the bulb to introduce either the zinc slurry or the $NaBH_4$ solution into the sample or standard. The metal hydride will produce a peak almost immediately. When the recorder pen returns to the baseline, remove the reaction vessel, empty, and proceed with the next sample.

8.5.6 Calculations

Draw a standard curve by plotting peak heights of standards versus concentration of standards. Measure the peak heights of the samples and read the concentration from the curve. Multiply these concentrations by the appropriate dilution factor.

8.5.7 Precision and Accuracy

Replicate 10 µg/liter samples exhibit a relative standard deviation of ±6% and a relative error of ±1.0%.

8.6 ANTIMONY ANALYSIS

8.6.1 Scope and Application

This method is applicable for the analysis of ammonium persulfate, hydrogen peroxide and dilute nitric acid and aqua regia solutions obtained from Level 1 samples.

8.6.2 Summary of Method

Organic antimony-containing compounds are decomposed by adding sulfuric and nitric acids and repeatedly evaporating the sample to fumes of sulfur trioxide. The antimony liberated, together with the inorganic antimony originally present, is subsequently reacted with potassium iodide and stannous chloride, and finally with sodium borohydride to form stibine. The stibine is removed from solution by aeration and swept by a flow of nitrogen into a hydrogen diffusion flame in an atomic absorption spectrometer. The gas sample absorption is measured at 217.6 nm. Since the stibine is freed from the original sample matrix, interferences in the flame are minimized.

8.6.3 Apparatus

- Atomic absorption spectrometer and recorder

  Refer to the manufacturers' manuals or procedures to optimize output of the instruments for the following parameters:

Grating	Ultraviolet
Wavelength	217.6 nm
Source (Electrodeless discharge or hollow cathode lamp)	Antimony
Burner	Three-slot burner or equivalent
Fuel	Hydrogen
Diluent	Nitrogen
Carrier	Nitrogen

- Stibine vapor analyzer (Figure 8-3) consisting of: 1) a 100 ml capacity three-neck round-bottom flask; 2) gas dispersion tube, coarse frit (Scientific Glass Apparatus Co. No. JG-8500 has been found satisfactory); and 3) 2 ml capacity medicine dropper, or 5 ml capacity automatic pipetter.

8.6.4 Reagents

- Antimony standard solution I, 1.00 ml = 100 µg Sb. Dissolve 274.3 mg antimony potassium tartrate, $(SbO)KC_4H_4O_6 \cdot 1/2H_2O$, in deionized water and dilute to 1 liter with deionized water.
- Antimony standard solution II, 1.00 ml = 10 µg Sb. Dilute 50.0 ml antimony solution I to 500.0 ml with deionized water.
- Antimony standard solution III, 1.0 ml = 0.10 µg Sb. Dilute 5.0 ml antimony standard solution II to 500.0 ml with deionized water. Prepare fresh before each use.
- Hydrochloric acid, conc. (sp gr 1.19).
- Nitric acid, conc. (sp gr 1.41).
- Potassium iodide solution, 15 g/100 ml. Dissolve 15 g KI in 100 ml deionized water. This solution is stable when stored in an amber bottle.
- Sodium borohydride solution, 4 g/100 ml. Dissolve 4 g $NaBH_4$ pellets in 100 ml deionized water (Alfa Products No. 14122 has been found satisfactory). Prepare fresh just before each use.
- Stannous chloride solution, 4.6 g per 100 ml conc. HCl. Dissolve 5 g $SnCl_2 \cdot H_2O$ in 100 ml conc. HCl (sp gr 1.19). This solution is stable if a few pieces of mossy tin are added to prevent oxidation.
- Sulfuric acid 9M. Cautiously, and with constant stirring and cooling, add 250 ml conc. H_2SO_4 (sp gr 1.84) to 250 ml deionized water.

8.6.5 Procedure

1) Prepare, in 150 ml beakers, a blank and sufficient standards containing from 0.0 to 1.5 µg Sb by diluting 0.0 to 15.0 ml portions of antimony standard solution III to 100 ml with deionized water.

2) To each beaker, add 7 ml 9M H_2SO_4 and 5 ml conc. HNO_3. Add a small boiling chip and carefully evaporate to fumes of SO_3. Maintain an excess of HNO_3 until all organic matter is destroyed as evidenced by a clear solution. This prevents

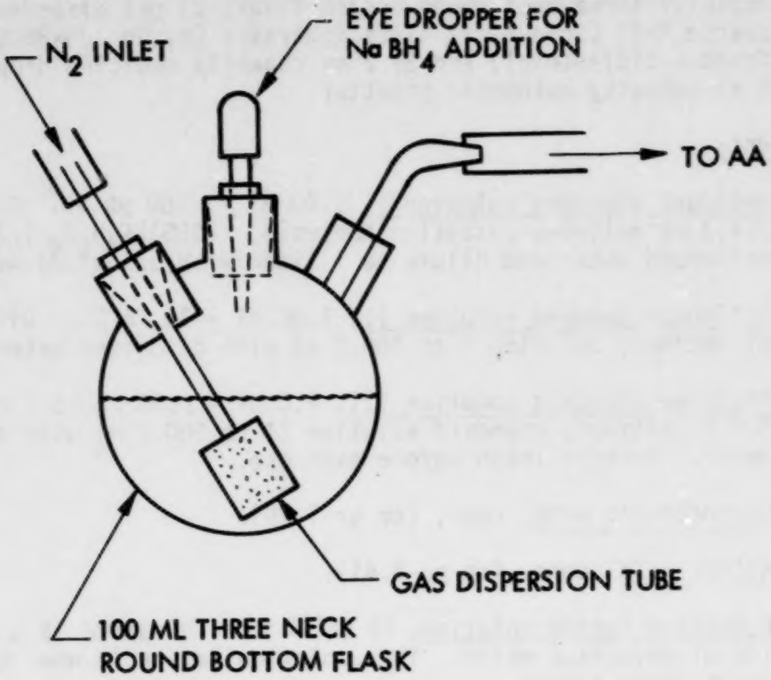
EYE DROPPER FOR
Na BH$_4$ ADDITION
N$_2$ INLET
TO AA
GAS DISPERSION TUBE
100 ML THREE NECK
ROUND BOTTOM FLASK

Figure 8-3. Hydride Evolution Apparatus

darkening of the solution and possible reduction and loss of antimony. Cool, add 25 ml deionized water, and again evaporate to fumes of SO_3 to expel oxides of nitrogen.

3) Cool, and adjust the volume of each beaker to approximately 50 ml with deionized water.

4) To each beaker, add successively, with thorough mixing after each addition, 4 ml conc. HCl, 1 ml KI solution, and 0.5 ml $SnCl_2$ solution. Allow about 15 minutes for reaction.

5) To set the N_2 carrier gas flow rate, place 55 ml of deionized water in the round-bottomed flask and put a rubber stopper in place of the medicine dropper. Increase the N_2 flow slowly until a maximum is reached which still avoids carrying liquid into the tubing leading to the AA instrument. Empty the flask and begin analyzing the samples by transferring the contents of each beaker, one at a time, to the flask and proceeding with the $NaBH_4$ reaction.

6) Fill the medicine dropper with ~1 ml $NaBH_4$ solution and insert into a one-hole rubber stopper that has been tightly fitted into the center neck of the three-neck round-bottom flask. Press the dropper and rubber stopper both in tightly.

7) Add the $NaBH_4$ solution all at once quickly to the sample solution. After the absorbance has reached a maximum and has returned to the baseline as measured by the AAS instrument, remove the flask. Rinse the gas dispersion tube in deionized water before proceeding to the next sample. Treat each succeeding sample, blank, and standard in a like manner.

8.6.6 Calculations

The µg of Sb in each sample aliquot is determined by comparison to a standard curve that plots absorbance vs. concentration. Exact reproducibility is not obtained; therefore, a standard must be prepared with each set of samples, compared with the standard curve and an appropriate correction made.

Determine the concentration of Sb as follows:

$$\text{Sb, ppm} = \frac{A \times \frac{B}{C}}{D}$$

Where:

A = µg Sb in sample, taken from calibration curve

B = Standard, known concentration µg Sb

C = Standard, µg Sb taken from calibration curve

D = Sample volume, ml

8.7 SULFATE ANALYSIS

8.7.1 Scope and Application

The turbidimetric procedure is designed to be used for Parr bomb combusted XAD-2 resins or fuels and for hot water and acid extracted particulate samples. For those cases in which both a hot water and an acid extraction is performed on aliquots of the same particulate sample, the sulfate analysis is to be performed on the hot water extract. The turbidimetric procedure may be performed on the acid extract of particulate samples. However, the values may be low because of incomplete formation of barium sulfate as a result of the high acid content in the sample. Color or suspended matter in large amounts will interfere with this method. Corrections for color can be made using appropriate blanks and suspended matter may be removed by filtration. Silica in excess of 500 mg/liter will interfere, and in waters containing large quantities of organic material it may not be possible to precipitate barium sulfate satisfactorily.

There are no ions other than sulfate in normal solutions that will form insoluble compounds with barium under strongly acid conditions. Determinations should be made at room temperature, which may vary over a range of 10°C without causing appreciable error.

The minimum detectable concentration is approximately 1 mg sulfate/liter.

8.7.2 Summary of Method

Sulfate ion is precipitated in a hydrochloric acid medium with barium chloride in such manner as to form barium sulfate crystals of uniform size. The absorbance of the barium sulfate suspension is measured by a transmission photometer and the sulfate ion concentration is determined by comparison of the reading with a standard curve.

8.7.3 Apparatus

- Magnetic stirrer. It is convenient to incorporate a timing device to permit the magnetic stirrer to operate for exactly 1 minute. The stirring speed should not vary appreciably. It is also convenient to incorporate a fixed resistance in series with the motor operating the magnetic stirrer to regulate the speed of stirring. If more than one magnet is used, they should be of identical shape and size. The exact speed of stirring is not critical, but it should be constant for each run of samples and standards and should be adjusted to about the maximum at which no splashing occurs.

- Photometer. One of the following is required with preference in the order given: nephelometer, such as Coleman Model #9; spectrophotometer, for use at 420 nm and providing a light path of 4-5 cm; filter photometer, equipped with a violet filter having maximum transmittance near 420 nm and providing a light path of 4-5 cm.
- Stopwatch, if the magnetic stirrer is not equipped with an accurate timer.
- Measuring spoon, capacity 0.2-0.3 ml.

8.7.4 Reagents

- Conditioning reagent. Mix 50 ml glycerol with a solution containing 30 ml concentrated HCl, 300 ml deionized water, 100 ml 95 percent ethyl or isopropyl alcohol, and 75 g sodium chloride.
- Barium chloride, crystals, 20-30 mesh.
- Standard sulfate solution. Prepare a standard sulfate solution by diluting 10.41 ml of standard 0.0200 N H_2SO_4 titrant to 100 ml with deionized water. Dissolve 147.9 mg anhydrous sodium sulfate, Na_2SO_4, in deionized water and dilute to 1000 ml.

8.7.5 Procedure

8.7.5.1 Formation of Barium Sulfate Turbidity

Measure 100 ml sample, or a suitable aliquot (record volumes) made up to 100 ml, into a 250 ml Erlenmeyer flask. Add exactly 5.00 ml conditioning reagent and mix in the stirring apparatus. While the solution is being stirred, add a spoonful of barium chloride crystals and begin the timing immediately. Stir for exactly 1 minute at a constant speed.

8.7.5.2 Measurement of Barium Sulfate Turbidity

Allow sample to set for 10 minutes prior to measurement. To measure the turbidity, pour some of the solution into the absorption cell of the photometer and record the absorbance.

8.7.5.3 Preparation of Calibration Curve

Estimate the sulfate concentration in the sample by comparing the turbidity reading with a calibration curve secured by carrying sulfate standards through the entire procedure. Space the standards at 5 mg/liter increments in the 0-40 mg/liter sulfate range. Above 40 mg/liter the accuracy of the method decreases and the suspensions of barium sulfate lose stability. Check reliability of the calibration curve by running a standard with every three or four unknown samples. Record results on analytical traveler.

8.7.5.4 Correction for Sample Color and Turbidity

Correct for the color and turbidity present in the original sample by running blanks from which the barium chloride is withheld. Obtain blank from diluted sample prior to addition of $BaCl_2$. Record blanks equivalent absorbance vs. deionized water.

8.7.6 Calculation

$$\text{Sulfate content (mg/liter)} = \frac{(A-B) \times 100 \text{ ml}}{\text{Sample Aliquot Volume, ml}}$$

where:

A = $SO_4^=$ content of sample interpolated from calibration curve, mg/liter (ppm)

B = $SO_4^=$ equivalent of blank interpolated from calibration curve, mg/liter (ppm)

8.8 CONTROLLED CONDENSATION SAMPLING TRAIN (CCS) - SAMPLE PREPARATION AND ANALYSIS

This section describes sample preparation and analysis procedures for CCS train samples. These procedures, summarized in Figure 8-4, include optional analyses for chloride and fluorides, along with the usual SO_3, SO_2, and particulate sulfate analyses.

8.8.1 Hot Water Extraction

8.8.1.1 Scope and Application

This procedure is to be used to prepare particulate samples for the determination of water soluble Cl, SO_4, and F anions. It is very similar to the aqua regia digestion procedure. However, it is necessary to maintain separate sets of glassware and Nalgene in order to avoid contamination of these samples with aqua regia.

8.8.1.2 Apparatus

- Distillation flasks, flat-bottom, 100 ml
- Condensers, Liebig or Allihn type
- Hot plate
- Volumetrics, 50 ml
- Filter funnels,
- Filter paper, Whatman No. 41

8.8.1.3 Reagent

Deionized water

8.8.1.4 Procedure

The weighed sample aliquot is placed in the distillation flask, 30 ml of deionized water are added, the condenser is attached, and the apparatus is secured over a hot plate. The water is refluxed for ∼1/2 hour at which time the apparatus is removed from the hot plate. While still hot, the solution in the distillation flask is filtered through a Whatman No. 41 filter into a volumetric. Wash several times with hot water, cool and dilute to volume. Label the volumetric and turn the sample in to the Sample Bank Manager.

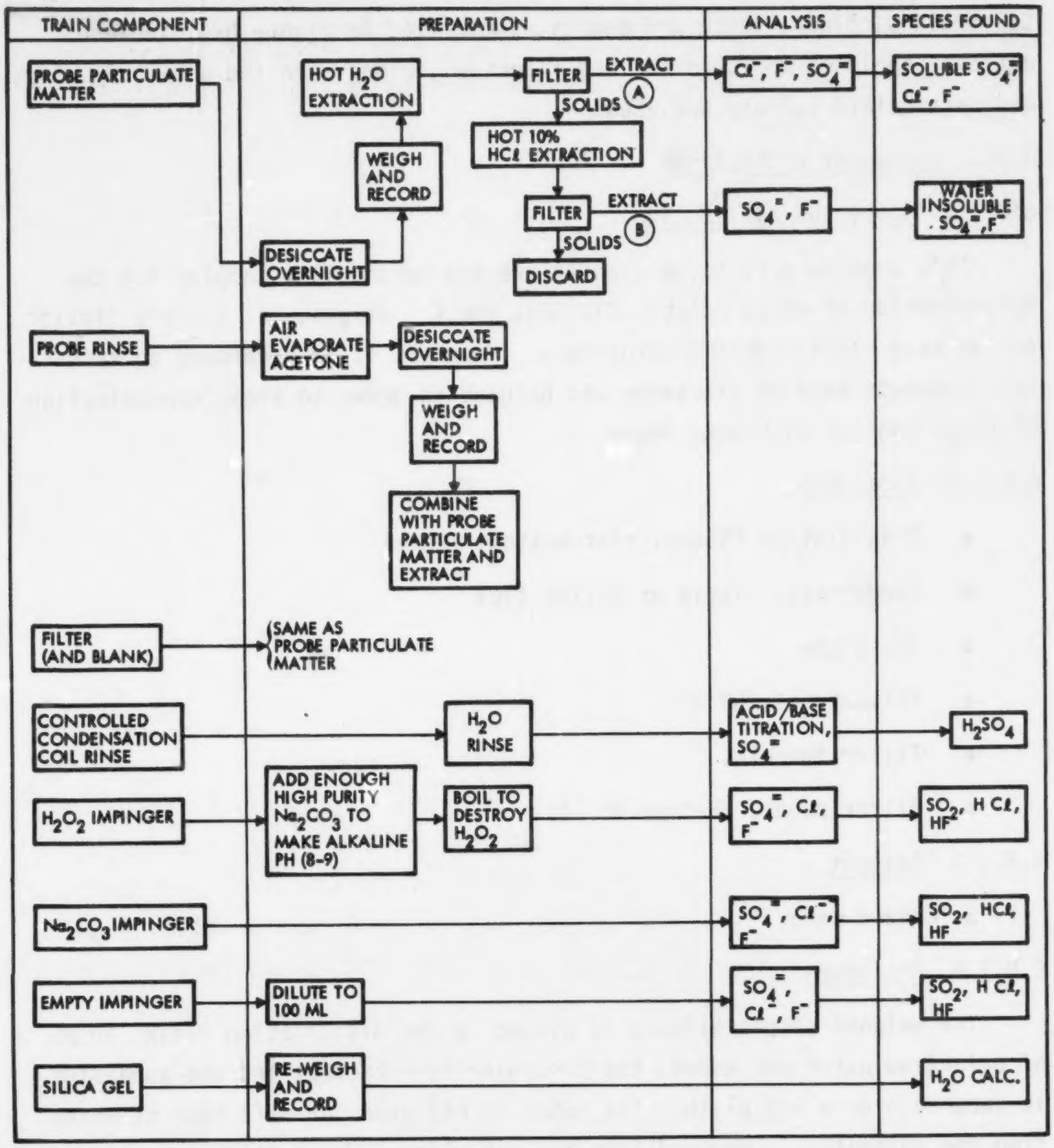
TRAIN COMPONENT
PREPARATION
ANALYSIS
SPECIES FOUND
PROBE PARTICULATE MATTER
HOT H2O EXTRACTION
FILTER
EXTRACT
A
SOLIDS
Cl⁻, F⁻, SO4⁼
SOLUBLE SO4⁼, Cl⁻, F⁻
WEIGH AND RECORD
HOT 10% HCl EXTRACTION
FILTER
EXTRACT
B
SOLIDS
SO4⁼, F⁻
WATER INSOLUBLE SO4⁼, F⁻
DESICCATE OVERNIGHT
DISCARD
PROBE RINSE
AIR EVAPORATE ACETONE
DESICCATE OVERNIGHT
WEIGH AND RECORD
COMBINE WITH PROBE PARTICULATE MATTER AND EXTRACT
FILTER (AND BLANK)
SAME AS PROBE PARTICULATE MATTER
CONTROLLED CONDENSATION COIL RINSE
H2O RINSE
ACID/BASE TITRATION, SO4⁼
H2SO4
H2O2 IMPINGER
ADD ENOUGH HIGH PURITY Na2CO3 TO MAKE ALKALINE PH (8-9)
BOIL TO DESTROY H2O2
SO4⁼, Cl, F⁻
SO2, HCl, HF
Na2CO3 IMPINGER
SO4⁼, Cl⁻, F⁻
SO2, HCl, HF
EMPTY IMPINGER
DILUTE TO 100 ML
SO4⁼, Cl⁻, F⁻
SO2, HCl, HF
SILICA GEL
RE-WEIGH AND RECORD
H2O CALC.

Figure 8-4. Analysis Scheme for Controlled Condensation Train Samples

8.8.2 Hot HCl Extraction

8.8.2.1 Scope and Application

This procedure is to be used to prepare particulate samples for the determination of water insoluble SO_4 and F. This procedure is nearly identical to Section 8.2.2. This glassware must not be interchanged with that used in Section 8.8.1.

8.8.2.2 Apparatus

- Distillation flasks, flat-bottom, 100 ml
- Condensers, Liebig or Allihn type
- Hot plate
- Volumetrics, 50 ml
- Filter funnels
- Filter paper, Whatman #41

8.8.2.3 Reagent

10 percent Hydrochloric acid solution

8.8.2.4 Procedure

The weighed sample aliquot is placed in the distillation flask, 30 ml of the hydrochloric acid solution is added, the condenser is attached, and the apparatus is secured over a hot plate. The solution is refluxed for 1/2 hour after which time the apparatus is removed from the hot plate. While still hot, filter the solution in the distillation flask through a Whatman #41 filter into a volumetric. Wash several times with 10 percent HCl solution, cool and dilute to volume. Label the volumetric and turn the sample in to the Sample Bank Manager.

8.8.3 Sulfuric Acid Analysis — Level 2 Analysis of CCS Coil Sample.

8.8.3.1 Scope and Application

Sulfuric acid in the CCS train coil condensate sample is determined by acid-base titration. All other CCS train samples are analyzed for sulfate by the turbidimetric method given in Section 8.7.

8.8.3.2 Summary of Method

The preferred method of analysis is the acid/base titration using Bromphenol Blue indicator. Carefully handle and store the samples in clean glassware and analyze them as soon as possible. Record all results on the laboratory data sheet.

Each acid/base indicator in this procedure will change color over a different pH range. For example:

Indicator	pH range	Color Change
Bromphenol Blue	3.0-4.6	yellow to blue
Phenolphthalein	8.2-10.0	colorless to pink

The point measured by the indicator is simply the point at which the color change occurs. The actual end point where exactly the right amount of acid and base have reacted (equivalence point) can be close to or far away from the indicator end point. Thus Bromphenol Blue is chosen for the NaOH + H_2SO_4 titration, since the equivalence point occurs at about pH 3. Phenolphthalein is used for the KHP + NaOH standardization titration because the equivalence point is near pH 7.

Even though the indicators have been selected to be as close as possible to the actual end point, a small difference still exists and is called the indicator blank. The indicator blank for phenolphtalein is the amount of NaOH required to change a specific amount of water containing a known number of drops of phenolphtalein pink. This value is subtracted from the milliliters used to titrate the sample.

The indicator blank from Bromphenol Blue is determined in the same way (known volume and number of drops) except that a standard acid (H_2SO_4) is used to backtitrate the indicator in distilled water to a yellow color. The number of milliequivalents used is added to the amount found titrating the sample.

NOTE

Blanks can vary with sample size and number of drops of indicator; therefore, determine the indicator blank under the same conditions in which the sample is titrated.

8.8.3.3 Apparatus

- Ten milliliter micro-buret, Kimble 17132F (A.H. Thomas, No. 1993-M-30 or equivalent)

- Four Erlenmeyer flasks with 28/15 ball-and-socket joint, 125 ml (Ace Glass Co., Louisville, Ky., No. 6975 or equivalent).

8.8.3.4 Reagents H_2SO4 Titration

- Carbon dioxide-free distilled water — Prepare all stock and standard solutions, and dilution water for standardization procedure, using distilled water which has a pH of not less than 6.0. If the water has a lower pH, it should be freshly boiled for 15 minutes and cooled to room temperature.

NOTE

> Deionized water may be substituted for distilled water provided that it has a conductance of less than 2 micro-ohms/cm and a pH greater than 6.0.

- NaOH pellets — Reagent grade.

- Stock 1.0 N NaOH — Dissolve 40 g of reagent grade NaOH in 1 liter of CO_2 free distilled water. Stored in a pyrex glass container with a tight-fitting rubber stopper.

- 0.0200 N NaOH — Dilute 20 ml of 1 N NaOH with CO_2 free distilled water to 1 liter. Store in a tightly rubber stoppered pyrex glass bottle protected from atmospheric CO_2 by a soda lime tube. For best results, prepare daily. This solution will be standardized against potassium biphthalate.

- Potassium biphthalate ($KHC_8H_4O_4$)-Anhydrous — Reagent grade.

- 0.0200 N potassium biphthalate (KHP) solution — Dissolve 4.085 g of dry (110°C for 1 hour) KHP into 1 liter of CO_2 free distilled water.

NOTE

> The normality of the KHP solution equals (wt. KHP)/204.2.

- Anhydrous ethyl alcohol — U.S.P. or equivalent.

- Phenolphthalein indicator solution — Dissolve 0.05 g of reagent grade phenolphthalein in 50 ml ethyl alcohol and dilute to 100 ml with CO_2 free water.

- Bromphenol Blue indicator solution — Dissolve 0.1 g in 7.5 ml of 0.02 N NaOH. Dilute to 250 ml with CO_2 free distilled water.

8.8.3.5 Procedures

Technique Since the end points for titrations are very color dependent, the end point will probably vary slightly for each operator's sense of color. To obtain the most accurate data, the following techniques should be employed in all titrations:

- Always add the same number of drops of indicator.
- Have the same operator do blank and sample.
- Always titrate to the same color intensity.
- Avoid parallax errors — keep eyes at the same level as the liquid meniscus and hold a white piece of paper behind it with a dark line horizontal to the table top.
- Remove air bubbles from buret tip prior to use.
- Never store reagent in buret. Always rinse out buret with a slight amount of titrant.
- Always record titrant type and volume used.

Standardization and Analysis

1) Pipet 10 ml of the 0.0200 N KHP solution into a 125 ml wide-mouth Erlenmeyer flask.

2) Add 3 drops of the Phenolphthlein indicator. With a swirling action the flask, titrate with 0.02 N NaOH solution until the first pink color stays. Record the volume and repeat from (1) in triplicate. Repeat this procedure using D.I. H_2O (blank).

3) Average the volume used to titrate the KHP solution. The true normality of the standard NaOH solution equals:

$$N = \left[(0.0200)\right] \frac{10\ \text{ml}}{(\text{ml titrant} - \text{ml blank})}$$

4) To titrate the H_2SO_4 in the condensation coil, probe, and filter rinses, pipet 10 ml of these solutions into a 125-ml Erlenmeyer flask. Add three drops of the Bromphenol Blue indicator to the solution and titrate to the blue end point. Triplicate analyses should be performed as well as an indicative blank. Be sure to use the same size aliquot and number of drops during the blank test titration. (See Paragraph 8.8.3.2). Remember this Bromophenol Blue sample blank is added to the sample value.

Calculations Using either the sulfate of acid/base titration, the concentration (ppm, V/V) of SO_3 as H_2SO_4 in the flue gas stream can be calculated.

1) From the Field Data Sheet obtain the average dry test meter temperature, volume of gas sampled and atmospheric pressure. Record these values on the Laboratory Data Sheet (Appendix B).

2) Using the Laboratory Data Sheet, insert the correct numbers into the following formula:

$$\text{ppm } H_2SO_4 = 1202.52 \left(\frac{NVT_m}{AV_m p}\right)$$

The result is ppm (v/v) H_2SO_4 at STP.

NOTE

This value can be 12 percent low due to fly ash present on the filter

Accuracy Check. In order to check the accuracy of the titrations performed on these samples, an independent check of the NaOH solution and titration method is required. An unknown standard sample of H_2SO_4 approximately 0.01 N should be analyzed by the lab personnel every couple of weeks. Analysis of the sample should be in triplicate and reported to 3 places (0.X Y Z). Analysis of this sample will provide information on the precision of the CCS titrations and accuracy of the results.

The procedure follows:

1) Take a 10 ml aliquot of the unknown standard.
2) Titrate in triplicate with Bromphenol Blue to the blue end point and record the number of milliliters used.
3) Determine the normality of the solution from:

$$N_A = \frac{N_B V_B}{V_A}$$

where

N_A = Normality of the acid
V_A = Volume acid aliquot taken (ml)
N_B = Normality of the base
V_B = Volume of the base used to titrate the sample (ml)

The results of the determination should not differ by more than ±10 percent within the triplicate numbers nor should the determined normality be off by more than ±10 percent.

If the values differ by more than 10 percent:

- Check the calculations and be sure the correct values have been used.
- Repeat the analysis.
- If the value is still off, restandardize the NaOH with KHP.
- Repeat the test.

8.9 FLUORIDE ANALYSIS

8.9.1 Scope and Application

This method is applicable to the measurement of fluoride in aqueous bulk liquids, solutions from H_2O_2 containing impinger samples, aqua regia extractions and Parr bomb combustions of SASS train samples.

Concentrations of fluoride from 0.1 up to 1000 ppm may be measured. Concentrations as low as 0.02 ppm can also be measured but a substantial length of time (on the order of several minutes) may be necessary for the electrode to stabilize and respond to the sample.

8.9.2 Summary of Method

Fluoride is determined potentiometrically using a selective ion fluoride electrode in conjunction with a standard single junction sleeve-type reference electrode and a pH meter having an expanded millivolt scale or a selective ion meter having a direct concentration scale for fluoride.

Sample pH should be between 5 and 9. Polyvalent cations of Si^{+4}, Fe^{+3} and Al^{+3} interfere by forming complexes with fluoride. The addition of a pH 5 total ionic strength adjustor buffer (TISAB II) containing a strong, chelating agent preferentially complexes aluminum (the most common interference), silicon, and iron and eliminates the pH problem.

The addition of TISAB II also provides a high total ionic strength background to help mask the difference in total ionic strengths between samples and standards. However, the TISAB II can not entirely compensate for this difference due to the very high and variable level of ionic strength in the Level 1 SASS samples. Thus a known addition technique is employed to eliminate the necessity of drawing different calibration curves for different types of samples.

8.9.3 Apparatus

- Electrometer (pH meter), with expanded mv scale, or a selective ion meter.
- Fluoride Ion Activity Electrode
- Reference electrode, single junction sleeve-type. Because all the SASS samples for fluoride measurement have an ionic strength above 0.2 M, the filling solution used is 4 M KCl (saturated with respect to silver ion by adding a dilute silver nitrate solution dropwise, until a milky silver chloride precipitate froms.)
- pH electrode
- Magnetic mixer, Teflon-coated stirring bar.

- Plastic lab ware — glassware cannot be used because of its reaction with fluoride.

  Beakers, 150 ml
  Volumetric flasks, 50 ml
  Pipets, 100 ml

- Graph paper — 4 cycle, semilog.

8.9.4 Reagents

- Total ionic strength adjustor buffer (TISAB II) — This solution can be obtained commercially (Orion # 94-09-09) or prepared in laboratory by adding 57 ml of glacial acetic acid, 58 g of sodium chloride and 2g of CDTA to approximately 500 ml deionized water in a 1 liter beaker(1). Stir to dissolve and cool to room temperature. Adjust pH of solution to between 5.0 and 5.5 with 5 N sodium hydroxide (about 150 ml will be required). Transfer solution to a 1 liter volumetric flask and dilute to the mark with deionized water.

- Sodium fluoride solution: 1.0 ml = 0.1 mg F. Dissolve 0.2210 g of sodium fluoride in deionized water and dilute to 1 liter in a volumetric flask. Store in chemical-resistant glass or polyethylene.

- NaOH, 5 N — Dissolve 20 g of NaOH in 100 ml of deionized water.

- HNO_3, 1:1 — Dilute 500 ml conc. HNO_3 to 1 liter with deionized water.

8.9.5 Procedure

8.9.5.1 Sample Preparation

Take a 5 ml aliquot of the sample and dilute it to ∿40 ml with deionized water in a 150 ml plastic beaker. Add 50 ml of TISAB II, mixing well. Measure the pH by pH electrode. Adjust the pH to 5.0 – 5.5 with 5 N NaOH. Bring the final total volume to 100 ml with deionized water.

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(1) CDTA is known as either cyclohexylene dinitrilo tetraacetic acid or 1,2 diaminocyclohexane N, N, N', N', — tetraacetic acid.

8.9.5.2 Calibration of the Electrode and the Meter

1) Read the manufacturer's instruction manual for the electrode and the meter to understand their operating procedures.

2) To measure the fluoride concentration using the known addition technique, the fluoride concentration of the sample must be known to within an order of magnitude, and a calibration curve must be prepared for that concentration range.

3) Prepare a series of standards in the range of 0.02 to 10 ppm by pipeting the appropriate volumes of stock fluoride solution into 50 ml volumetric flasks. Add 0.5 ml of 1:1 HNO_3 to simulate the sample matrix of most SASS samples. Add deionized water to bring the volume to 50 ml.

4) Measure the potential of these standards as described in Section 8.9.5.3.

5) Using semilog graph paper, plot the concentration of fluoride in mg/liter on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale.

6) From the calibration curve, read the value of the slope (the change in potential observed when the concentration changes by a factor of ten). Correct electrode and meter operation is indicated by a slope of 58 ± 1 mV, at a temp of 20^{o} – $25^{o}C$. If the change in potential is not within this range, refer back to the manufacturer's manual for suggested corrective actions.

8.9.5.3 Measurement of Potential

1) Place 50.0 ml of sample or standard solution and 50.0 ml of buffer in a beaker.

2) Place on a magnetic stirrer and mix at medium speed. Use the nominal values of the standards in calibrating the electrodes, e.g., if a 10 ppm standard is diluted with TISAB, the reading obtained is still designated "10 ppm".

3) Immerse the electrodes in the solution and observe the meter reading while mixing. The electrodes must remain in the solution for at least three minutes or until the reading has stabilized. At concentrations under 0.5 ppm F, it may require as long as five minutes to reach a stable meter reading: higher concentrations stabilize more quickly.

4) Record the potential measurement for each unknown sample and convert the potential reading to the fluoride ion concentration of the unknown using the standard curve.

8.9.5.4 Known Addition Procedure

1) Measure the potential of the sample solution at 25°C as described above. Leave the electrode in the solution.

2) Prepare a 50 ml standard solution containing about 10 times as much fluoride as the sample. Add 50 ml TISAB II. (Use the nominal value of the standard in calculating results; e.g., if a 10 ppm standard is dilute with TISAB, the standard is still designated "10 ppm".

3) Pipet 10 ml of this standard into the sample solution and stir well.

4) Record this potential measurement also.

8.9.6 Calculations

Calculate the difference in potential, ΔE, after the addition of the fluoride standard.

From Table 8.2, find the concentration ratio, Q, that corresponds to the change in potential, ΔE. To determine the original total sample concentration, multiply Q by the concentration of the added standard:

$$C_o = fQC_s$$

where:

C_o = total sample concentration
Q = reading from known addition table
C_s = concentration of added standard
f = dilution factor, e.e., if a 5 ml sample aliquot is taken and diluted to 50 ml, then f = 10.

Table 8-2. Fluoride Analysis: "Addition Procedure" Table for Q vs. ΔE (millivolts) at 25°C for 10% Volume Change

ΔE	Q	ΔE	Q	ΔE	Q	ΔE	Q
-5.0	0.297	10.0	0.160	-20.0	0.0716	30.0	0.0394
5.1	0.293	10.2	0.157	20.2	0.0707	30.2	0.0390
5.2	0.288	10.4	0.154	20.4	0.0698	30.4	0.0386
5.3	0.284	10.6	0.151	20.6	0.0689	30.6	0.0382
5.4	0.280	10.8	0.148	20.8	0.0680	30.8	0.0378
5.5	0.276	11.0	0.145	21.0	0.0671	31.0	0.0374
5.6	0.272	11.2	0.143	21.2	0.0662	31.2	0.0370
5.7	0.268	11.4	0.140	21.4	0.0654	31.4	0.0366
5.8	0.264	11.6	0.137	21.6	0.0645	31.6	0.0362
5.9	0.260	11.8	0.135	21.8	0.0637	31.8	0.0358
6.0	0.257	12.0	0.133	22.0	0.0629	32.0	0.0354
6.1	0.253	12.2	0.130	22.2	0.0621	32.2	0.0351
6.2	0.250	12.4	0.128	22.4	0.0613	32.4	0.0347
6.3	0.247	12.6	0.126	22.6	0.0606	32.6	0.0343
6.4	0.243	12.8	0.123	22.8	0.0598	32.8	0.0340
6.5	0.240	13.0	0.121	23.0	0.0591	33.0	0.0336
6.6	0.237	13.2	0.119	23.2	0.0584	33.2	0.0333
6.7	0.234	13.4	0.117	23.4	0.0576	33.4	0.0329
6.8	0.231	13.6	0.115	23.6	0.0569	33.6	0.0326
6.9	0.228	13.8	0.113	23.8	0.0563	33.8	0.0323
7.0	0.225	14.0	0.112	24.0	0.0556	34.0	0.0319
7.1	0.222	14.2	0.110	24.2	0.0549	34.2	0.0316
7.2	0.219	14.4	0.108	24.4	0.0543	34.4	0.0313
7.3	0.217	14.6	0.106	24.6	0.0536	34.6	0.0310
7.4	0.214	14.8	0.105	24.8	0.0530	34.8	0.0307
7.5	0.212	15.0	0.103	25.0	0.0523	35.0	0.0304
7.6	0.209	15.2	0.1013	25.2	0.0517	36.0	0.0289
7.7	0.207	15.4	0.0997	25.4	0.0511	37.0	0.0275
7.8	0.204	15.6	0.0982	25.6	0.0505	38.0	0.0261
7.9	0.202	15.8	0.0967	25.8	0.0499	39.0	0.0249
8.0	0.199	16.0	0.0952	26.0	0.0494	40.0	0.0237
8.1	0.197	16.2	0.0938	26.2	0.0488	41.0	0.0226
8.2	0.195	16.4	0.0924	26.4	0.0482	42.0	0.0216
8.3	0.193	16.6	0.0910	26.6	0.0477	43.0	0.0206
8.4	0.190	16.8	0.0897	26.8	0.0471	44.0	0.0196
8.5	0.188	17.0	0.0884	27.0	0.0466	45.0	0.0187
8.6	0.186	17.2	0.0871	27.2	0.0461	46.0	0.0179
8.7	0.184	17.4	0.0858	27.4	0.0456	47.0	0.0171
8.8	0.182	17.6	0.0846	27.6	0.0450	48.0	0.0163
8.9	0.180	17.8	0.0834	27.8	0.0445	49.0	0.0156

Table 8-2. Fluoride Analysis: "Addition Procedure" Table for Q vs. ΔE (millivolts) at 25°C for 10% Volume Change (Continued)

ΔE	Q	ΔE	Q	ΔE	Q	ΔE	Q
9.0	0.178	18.0	0.0822	28.0	0.0440	50.0	0.0149
9.1	0.176	18.2	0.0811	28.2	0.0435	51.0	0.0143
9.2	0.174	18.4	0.0799	28.4	0.0431	52.0	0.0137
9.3	0.173	18.6	0.0788	28.6	0.0426	53.0	0.0131
9.4	0.171	18.8	0.0777	28.8	0.0421	54.0	0.0125
9.5	0.169	19.0	0.0767	29.0	0.0417	55.0	0.0120
9.6	0.167	19.2	0.0756	29.2	0.0412	56.0	0.0115
9.7	0.165	19.4	0.0746	29.4	0.0408	57.0	0.0110
9.8	0.164	19.6	0.0736	29.6	0.0403	58.0	0.0105
9.9	0.162	19.8	0.0726	29.8	0.0399	59.0	0.0101

8.10 CHLORIDE ANALYSIS

8.10.1 Scope and Application

This method is applicable to the measurement of chloride in aqueous bulk liquids, solutions from H_2O_2 impingers, module condensates and rinses, hot water extractions of particulates and Parr bomb combustions of Level 1 samples. Chloride concentrations from 0.05 to 1000 ppm may be measured.

8.10.2 Summary of Method

Chloride is determined potentiometrically using a solid state selective ion chloride electrode in conjunction with a double junction reference electrode and a pH meter having an expanded millivolt scale or a selective ion meter having a direct concentration scale for chloride. The solid state electrode is used because it is not sensitive to the higher levels of nitrate, sulfate or bicarbonate which could be present in several of the Level 1 samples. This method does require that the sample and standards have the same total ionic strength. Because Level 1 samples can have a very high and variable level total ionic strength, a known addition technique is employed to eliminate the necessity of drawing different calibration curves for different types of samples.

8.10.3 Apparatus

- Electrometer (pH meter), with expanded mv scale, or a selective ion meter.
- Chloride ion activity electrode, solid state
- Reference electrode, double junction
- Magnetic mixer, Teflon coated stirring bar
- Beakers, 150 ml
- Pipets
- Volumetric flasks, 100 ml
- Graph paper, 4 cycle, semilog.

8.10.4 Reagents

- Sodium chloride stock solution: 1.0 ml = 1.0 mg Cl^- Dissolve 2.037 g of sodium chloride in deionized water and dilute to 1 liter in a volumetric flask.
- HNO_3, 1:1 — Dilute 500 ml conc. HNO_3 to 1 liter with deionized water.

8.10.5 Procedure

8.10.5.1 Calibration of the Electrode and the Meter

1) Read the manufacturer's instruction manual for the electrode and the meter to understand their operating procedures.

2) To measure the chloride concentration using the known addition technique, the chloride concentration of the sample must be known to within an order of magnitude. A calibration curve has to be drawn.

3) Prepare a series of standards in the range of 0.05 to 100 ppm by pipeting the appropriate volumes of stock chloride solution into 100 ml volumetric flasks. Add 0.5 ml of 1:1 HNO_3 to simulate the sample matrix of most SASS samples. Add deionized water to bring the volume to 100 ml.

4) Measure the potential of these standards as described in Section 8.10.5.2.

5) Using semilog graph paper, plot the concentration of chloride in mg/liter on the log axis versus the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale.

6) From the calibration curve, read the value of the slope (the change in potential observed when the concentration changes by a factor of ten). Correct electrode and meter operation is indicated by a slope of 58 ± 1 mV, at a temp of 20^o-25^oC. If the change in potential is not within this range, refer back to the manufacturer's manual for suggested corrective actions.

8.10.5.2 Measurement of Potential

1) Put 50 ml of sample or an aliquot diluted to 100 ml into a 150 ml beaker.

2) Place on magnetic stirrer and stir at medium speed.

3) Immerse the electrodes in the solution and observe the meter reading while mixing. The electrodes must remain in the solution for at least three minutes or until the reading has stabilized. At concentrations under 0.5 ppm Cl, it may require as long as five minutes to reach a stable meter reading: higher concentrations stabilize more quickly.

4) Record the potential measurement for each unknown sample and convert the potential reading to the chloride ion concentration of the unknown using the calibration curve.

8.10.5.3 Known Addition Procedure

1) Measure the potential of the sample solution at 25°C as described above. Leave the electrode in the solution.

2) Prepare a standard solution containing about 10 times as much chloride as the sample.

3) Pipet 5 ml of this standard into the sample solution and stir well.

4) Record this potential measurement also.

5) Perform this procedure with a blank of 50 ml deionized water also.

8.10.6 Calculations

Calculate the difference in potential, ΔE, after the addition of the chloride standard.

From Table 8.3, find the concentration ratio , Q, that corresponds to the change in potential, ΔE. To determine the original total sample concentration, multiply Q by the concentration of the added standard:

$$C_o = \frac{50\ (Q_s C_s - Q_b C_b)}{V}$$

where:

C_o = total sample concentration

Q_s = reading from known addition table for the sample

C_s = concentration of added standard

V = volume of sample aliquot, ml

Table 8-3. Chloride Analysis: "Addition Procedure" Table for Q vs. ΔE (millivolts) at 25°C for 10% Volume Change

ΔE	Q	ΔE	Q	ΔE	Q	ΔE	Q
+2.4	52.6	4.5	0.322	13.0	0.121	27.0	0.0466
+2.3	17.2	4.6	0.319	13.2	0.119	27.2	0.0461
+2.2	10.3	4.7	0.312	13.4	0.117	27.4	0.0456
+2.1	7.32	4.8	0.307	13.6	0.115	27.6	0.0450
+2.0	5.68	4.9	0.302	13.8	0.113	27.8	0.0445
+1.9	4.63	5.0	0.297	14.0	0.112	28.0	0.0440
+1.8	3.91	5.1	0.293	14.2	0.110	28.2	0.0435
+1.7	3.38	5.2	0.288	14.4	0.108	28.4	0.0431
+1.6	2.98	5.3	0.284	14.6	0.106	28.6	0.0426
+1.5	2.66	5.4	0.280	14.8	0.105	28.8	0.0421
+1.4	2.40	5.5	0.276	15.0	0.103	29.0	0.0417
+1.3	2.19	5.6	0.272	15.2	0.1013	29.2	0.0412
+1.2	2.01	5.7	0.268	15.4	0.0997	29.4	0.0408
+1.1	1.86	5.8	0.264	15.6	0.0982	29.6	0.0403
+1.0	1.72	5.9	0.260	15.8	0.0967	29.8	0.0399
+0.9	1.61	6.0	0.257	16.0	0.0952	30.0	0.0394
+0.8	1.51	6.1	0.253	16.2	0.0938	30.2	0.0390
+0.7	1.42	6.2	0.250	16.4	0.0924	30.4	0.0386
+0.6	1.34	6.3	0.247	16.6	0.0910	30.6	0.0382
+0.5	1.27	6.4	0.243	16.8	0.0897	30.8	0.0378
+0.4	1.21	6.5	0.240	17.0	0.0884	31.0	0.0374
+0.3	1.15	6.6	0.237	17.2	0.0871	31.2	0.0370
+0.2	1.09	6.7	0.234	17.4	0.0858	31.4	0.0366
+0.1	1.05	6.8	0.231	17.6	0.0846	31.6	0.0362
0.0	1.00	6.9	0.228	17.8	0.0834	31.8	0.0358
-0.1	0.959	7.0	0.225	-18.0	0.0822	32.0	0.0354
0.2	0.921	7.1	0.222	18.2	0.0811	32.2	0.0351
0.3	0.886	7.2	0.219	18.4	0.0799	32.4	0.0347
0.4	0.853	7.3	0.217	18.6	0.0788	32.6	0.0343
0.5	0.822	7.4	0.214	18.8	0.0777	32.8	0.0340
0.6	0.794	7.5	0.212	19.0	0.0767	33.0	0.0336
0.7	0.767	7.6	0.209	19.2	0.0756	33.2	0.0333
0.8	0.742	7.7	0.207	19.4	0.0746	33.4	0.0329
0.9	0.718	7.8	0.204	19.6	0.0736	33.6	0.0326
1.0	0.696	7.9	0.202	19.8	0.0726	33.8	0.0323
1.1	0.675	8.0	0.199	20.0	0.0716	34.0	0.0319
1.2	0.655	8.1	0.197	20.2	0.0707	34.2	0.0316
1.3	0.637	8.2	0.195	20.4	0.0698	34.4	0.0313
1.4	0.619	8.3	0.193	20.6	0.0689	34.6	0.0310

Table 8-3. Chloride Analysis: "Addition Procedure" Table for Q vs. ΔE (millivolts) at 25^{o}C for 10% Volume Change (Continued)

ΔE	Q	ΔE	Q	ΔE	Q	ΔE	Q
1.5	0.602	8.4	0.190	20.8	0.0680	34.8	0.0307
1.6	0.586	8.5	0.188	21.0	0.0671	35.0	0.0304
1.7	0.571	8.6	0.186	21.2	0.0662	36.0	0.0289
1.8	0.556	8.7	0.184	21.4	0.0654	37.0	0.0275
1.9	0.542	8.8	0.182	21.6	0.0645	38.0	0.0261
2.0	0.529	8.9	0.180	21.8	0.0637	39.0	0.0249
2.1	0.516	9.0	0.178	22.0	0.0629	40.0	0.0237
2.2	0.504	9.1	0.176	22.2	0.0621	41.0	0.0226
2.3	0.493	9.2	0.174	22.4	0.0613	42.0	0.0216
2.4	0.482	9.3	0.173	22.6	0.0606	43.0	0.0206
2.5	0.471	9.4	0.171	22.8	0.0598	44.0	0.0196
2.6	0.461	9.5	0.169	23.0	0.0591	45.0	0.0187
2.7	0.451	9.6	0.167	23.2	0.0584	46.0	0.0179
2.8	0.441	9.7	0.165	23.4	0.0576	47.0	0.0171
2.9	0.432	9.8	0.164	23.6	0.0569	48.0	0.0163
3.0	0.423	9.9	0.162	23.8	0.0563	49.0	0.0156
3.1	0.415	10.0	0.160	24.0	0.0556	50.0	0.0149
3.2	0.407	10.2	0.157	24.2	0.0549	51.0	0.0143
3.3	0.399	10.4	0.154	24.4	0.0543	52.0	0.0137
3.4	0.391	10.6	0.151	24.6	0.0536	53.0	0.0131
		10.8	0.148	24.8	0.0530	54.0	0.0125
3.5	0.384	11.0	0.145	25.0	0.0523	55.0	0.0120
3.6	0.377	11.2	0.143	25.2	0.0517	56.0	0.0115
3.7	0.370	11.4	0.140	25.4	0.0511	57.0	0.0110
3.8	0.363	11.6	0.137	25.6	0.0505	58.0	0.0105
3.9	0.357	11.8	0.135	25.8	0.0499	59.0	0.0101
4.0	0.351	12.0	0.133	26.0	0.0494		
4.1	0.345	12.2	0.130	26.2	0.0488		
4.2	0.339	12.4	0.128	26.4	0.0482		
4.3	0.333	12.6	0.126	26.6	0.0477		
4.4	0.327	12.8	0.123	26.8	0.0471		

Q_b = reading from known addition table for the blank

C_b = concentration of standard added to the blank

8.11 PHENOLDISULFONIC ACID PROCEDURE FOR DETERMINATION OF NITROGEN OXIDES (EPA Method 7)

8.11.1 Scope

8.11.1.1 Application

This procedure is dictated for the analysis of nitrogen oxides (NOx) from stationary sources by the Environmental Protection Agency.[1] The samples received by the laboratory have been obtained by rapidly pulling the sample gas into an evacuated 2 liter borosilicate vessel which contains 25 ml of an absorbing solution. The sample gas will have been in contact with the 0.003 percent H_2O_2 in 0.1 NH_2SO_4 absorbing solution for a minimum of 16 hours to ensure complete conversion of NO_x to the nitrate ion.

The laboratory analysis requires first quantitatively transferring the sample solution to an appropriate container, neutralizing it with NaOH and evaporating it to dryness. The residue is then reacted with phenoldisulfonic acid (PDSA), diluted and made alkaline with NH_4OH. This results in the formation of a yellow nitro chromogen which can be measured spectrophotometrically at 405 nm.

8.11.1.2 Range

The range of the method is stated to be 2 to 400 mg NO_x as NO_2 per dry standard cubic meter, although 16 hours reaction time may not be adequate for a complete reaction to occur whenever the NOx concentration is below 200 ppm.[2]

8.11.1.3 Interferences

HCl, which will be present in stack gases from coal burning facilities, will interfere with this determination due to the formation of NOCl. Method 7 does not offer any means of eliminating this interference. Martens, *et al*., have described procedural modifications which can be used to minimize this problem.[2]

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[1] "Method 7 - Determination of Nitrogen Oxide Emissions from Stationary Sources." Federal Register, Vol. 41, No. 111, June 8, 1976. pp. 23085-23087.

[2] Martens, H.H., Dee, L.A., Nakamura, J.T., and Jaye, F.C., *Environ. Sci. Tech*., Vol *7*, December, 1973. pp. 1152-1154.

Unacceptable variability in absorbance readings can also result from solution turbidity, CO_2 evolution and the loss of nitro-PDSA by adsorption onto the glass evaporating dish.

Filtering will remove turbidity. CO_2 evolution can be minimized by slow, careful neutralization of the absorbing solution with NaOH. Also, avoiding the addition of excess NaOH enhances the recovery and makes the evaporation easier. Using new smooth evaporating dishes reduces the possibility of nitro-PDSA absorbing or reacting with the silicates in the glass.

8.11.2 Apparatus

- Graduated cylinder-50 ml with 1-ml divisions
- Storage container-Leak-free polyethylene bottles
- Wash bottle- Teflon
- Glass stirring rod
- pH test paper-Litmus paper is sufficient
- Volumetric pipets-Two 1-ml, two 2-ml, one 3-ml, one 4-ml and two 10-ml, and one 25-ml for each sample and standard.
- Borosilicate Evaporating dishes - 175 to 250 ml capacity with lip for pouring, one for each sample and each standard. N.B. Use only new borosilicate glass dishes. Old dishes may be etched and provide sites for nitro-PDSA to be absorbed and lost.
- Steam bath. (A hot plate is not acceptable.)
- Dropping pipet or dropper-Three required
- Teflon policeman-One for each sample and each standard
- Graduated cylinder-100-ml with 1-ml divisions

- Volumetric flasks-50-ml (one for each sample). 100-ml (one for each sample, each standard and one for the working standard KNO_3 solution), and one 1000-mℓ.
- Spectrophotometer-To measure absorbance at 405 nm.
- Graduated pipet-10-ml, with 0.1-ml divisions.
- Analytical balance-To measure to 0.1 mg.

8.11.3 Reagents

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use best available grade.

- Absorbing solution-Cautiously add 2.8 ml concentrated H_2SO_4 to 1 liter of deionized, distilled water. Mix well and add 6 ml of 3 percent hydrogen peroxide, freshly prepared from 30 percent hydrogen peroxide solution. The solution should be used within one week of its preparation. Do not expose to extreme heat or direct sunlight.
- Fuming sulfuric acid-15 to 18 percent by weight free sulfur trioxide. Handle with caution.
- Phenol-White solid.
- Sulfuric acid-Concentrated, 95 percent minimum assay. Handle with caution.
- Potassium nitrate-Dried at 105-110°C for minimum of two hours just prior to preparation of standard solution.
- Standard solution-Dissolve exactly 2.1980 of dried potassium nitrate (KNO_3) in deionized, distilled water and dilute to 1 liter with deionized, distilled water in a 1000-ml volumetric flask. For the working standard solution, dilute 10 ml of the standard solution to 100 ml deionized distilled water. One ml of the working standard solution is equivalent to 100 μg nitrogen dioxide (NO_2).
- Water-Deionized and distilled.
- Phenoldisulfonic acid solution-Dissolve 25 g of pure white phenol in 150 ml concentrated sulfuric acid on a steam bath. Cool, add 75 ml fuming sulfuric acid, and heat at 100°C (212°F) for 2 hours. Store in a dark, stoppered bottle.

8.11.4 Procedure

a) Note Level of liquid in container and confirm whether or not any sample was lost during shipment by noting this on analytical data sheet.

b) Transfer the contents of the shipping container to a 50-ml volumetric flask, rinse the container twice with 5-ml portions of deionized, distilled water, add the rinse water to the flask and dilute to the mark with deionized, distilled water.

c) Mix thoroughly and pipet a 25 ml aliquot into the evaporating dish.

d) Evaporate the solution to dryness on a steam bath (use only a steam bath — a hot plate is unacceptable).

e) Add 2 ml phenoldisulfonic acid to the dried residue and triturate thoroughly with a Teflon policeman. Be sure the solution contacts all the residue.

f) Add 1 ml deionized, distilled water and 4 drops of concentrated H_2SO_4.

g) Heat the solution on a steam bath for 3 minutes with occasional stirring.

h) Cool, add 20 ml deionized, distilled water and mix well.

i) Add 15 ml concentrated ammonium hydroxide slowly, preferably dropwise, with constant stirring.

j) If the sample contains solids, filter through Whatman No. 41 filter paper into a 100-ml volumetric flask; rinse the evaporating dish with three 5-ml portions of deionized, distilled water and add these to the filter. Wash the filter with at least three 15-ml portions of deionized, distilled water. Add the filter washings to the contents of the volumetric flask and dilute to the mark with deionized, distilled water. If solids are absent, transfer the solution directly to the 100-ml volumetric flask, dilute to the mark with deionized distilled water and mix thoroughly.

h) Measure the absorbance of the solution at 405 nm using the blank solution as a zero reference. Dilute the sample and the blank with a suitable amount of deionized, distilled water if absorbance exceeds the absorbance of the 400 μg NO_2 standard.

8.11.5 Calibration

a) Add 0.0 ml, 1.0 ml, 2.0 ml, 3.0 ml and 4.0 ml of the KNO_3 working standard solution (1 ml ± 100 μg NO_2) to a series of evaporating dishes.

b) To each, add 25 ml of absorbing solution, 10 ml deionized, distilled water and N NaOH dropwise until the solution is basic to litmus. (Avoid adding excess base.)

c) Follow the analysis procedure given in the preceding section, beginning with step (d) to determine the spectrophotometer calibration factor.

d) Calculate the spectrophotometer calibration factor Kc as follows.

$$K_c = 100\,\frac{A1+2A_2+3A_3 4A_4}{A_1{}^2+A_2{}^2+A_3{}^2+A_4{}^2}$$

where:

K_c = Calibration factor

A_1 = Absorbance of the 100μg NO_2 standard

A_2 = Absorbance of the 200μg NO_2 standard

A_3 = Absorbance of the 300μg NO_2 standard

A_4 = Absorbance of the 400μg NO_2 standard

e) Repeat this calibration on every day samples are analyzed.

8.11.6 Calculations

Carry out the calculations, retaining at lease one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

Total μg NO_2 per sample.

$$m = 2K_c\,AF$$

where:

A = Absorbance of sample

F = Dilution factor (i.e., 25/5, 25/10, etc., required only if sample dilution was needed to reduce the absorbance into range of calibration)

K = Spectrophotometer calibration factor

m = Mass of NO_x as NO_2 in gas sample, μg

NOTE

If other than a 25-ml aliquot is used for analyses, the factor 2 must be substituted by a corresponding factor.

APPENDIX A

CRITERIA FOR A COST-EFFECTIVE LEVEL 1 QUALITY ASSURANCE PROGRAM

APPENDIX A

This appendix discusses a cost-effective quality assurance program for the EACCS Level 1 testing. The approach presumes that currently-maintained test procedures and consistently trained personnel are available. The quality assurance activities consist of monitoring compliance with the established procedures and verifying the reproducibility of the data produced from application of these procedures. The program is made cost-effective by formulating Q.A. limits and emphases which are consistent with the Level 1 accuracy requirement. Basically, this approach differs from the approach used in Level 2 or Level 3 in that the emphasis is centered on maintaining reasonable confidence that most data will fall within the relatively broad limits of Level 1 testing, as opposed to tightening controls so that maximum accuracy is obtained from a test. For example, a Level 1 quality audit will verify that precautions are effective against repeated occurrence of gross errors (i.e., errors much beyond the desired accuracy factor of 3). An appropriate Level 2 or Level 3 quality audit would, in addition, verify that testing was within acceptable limits of standard materials or carefully performed reference tests. Early reduction in the quality testing needed to verify the quality limits are being met is also possible because the requirements are less stringent than for Level 2 or Level 3 tests. This technique is discussed in this appendix for the program replicate testing and repeated testing of "blank" reagents.

A. AUDITING LEVEL 1 TESTS

The Level 1 EACCS program is primarily intended as a screening mechanism for potential problem sources of pollutants, and an accuracy factor of 3 has been used to express acceptability of sampling and analysis for the Level 1 testing. An accuracy factor of three is liberal for many accepted analytical test procedures and methods of sampling. For example, 2/3 of the analytical tests in Reference (a)* are precise (2 x coefficient of variation) to better than ± 30 percent, and biases, if present, are corrected by various means such as calibration curves, etc. Thus the analytical accuracy factor for these tests would be approximately 1.4. Sampling error, i.e., the taking of a non-representative sample because of non-representative conditions by poor identification of isokinetic points in stacks, insufficiently flushed water lines, etc., is probably less than a factor of 2 because of the probability that severely atypical conditions will be noted by experienced personnel and because inherent random mixing tends to reduce the effects of stratification, a major cause of non-representative samples. Thus, except for specific tests or methods which may be inadequately characterized at this time, the procedures and methods to be used for Level 1 testing can be assumed to be inherently capable of factor of 3 accuracy.

---

*Reference (a): Guidelines for Environmental Assessment Quality Assurance Program, R.T.I. (Rough Draft), September 1976.

This is an important assumption. It means that normal day-to-day sampling, material control testing, and standardization metrology are adequately controlled by personnel selection, training programs, equipment controls and supervision. In other words, existing practices, equipment and personnel are "state-of-the-art" and controlled by adequate guidelines and procedures to Level 1 accuracy. If this is so, the Level 1 quality program should aim to reduce the occurrence of excursions from procedures in factors which will cause undetected variation rather than verify the adequacy of the procedures to produce Level 1 accuracy.

To do this, the quality program must identify and emphasize the sources of error which are most likely to cause extreme variation. Examples of such gross sources of error are:

- contamination
- cumulative buildup in sampling equipment
- sample loss or concentration
- transposed data numerals
- erroneously marked sample identity
- incorrect physical units or loss of digits in recorded parameters.

In addition, particular procedures may have specific key items. Examination of this list shows cleanup, mathematical procedures, and spillage to be the features of each procedure needing quality assurance, rather than traceability of reagents, routine instrument settings, etc.

It is therefore assumed that Level 1 accuracy will be most probably exceeded by human error in following procedural steps involving potential error sources similar to those above, which can be identified from the procedures.

If it is assumed further, that procedures are about equal in quality control sophistication, the frequency of deviation from procedures will be more related to an individual than to the procedure itself. Thus, if we then audit a given total number of critical procedural steps for an individual (to be anonymous), we have a sample from which to estimate the probable number of "failures" (critical procedure deviations) associated with the testing by that individual. For example, using the binomial population assumption for "successes" and "failures", the reliability of the audited individual could be estimated to be 0.98 with 90 percent confidence with no deviation in 114 points of audit, or with one deviation, in 193 points of audit. It must be noted that, hopefully, not all critical procedural excursions will exceed Level 1 accuracy, consequently, a minimum reliability of 0.98 may in fact represent a much higher actual reliability in terms of the data reported being within Level 1 accuracy.

For some procedures, the assumption of inherent Level 1 accuracy may not be valid. Thus, in addition to the above audit, some characterization of accuracy and precision will be needed. These procedures will then be evaluated by using "spiked" samples, blind samples, standards, etc. If Level 1 accuracy is not demonstrated, it will be necessary to study procedural detail to devise a tightened control for that procedure. Subsequent audits will then include auditing the application of these tightened controls.

B. SELECTION OF NUMBER OF BLANKS FOR A REAGENT USED REPEATEDLY FROM THE SAME CONTAINER

B.1 Nature of the Problem

Repeated blanks on the same container protect against probable gradual contamination of the container during usage. This protection may be excessive in terms of Level 1 accuracy when adequate chemical precautions are taken. A more serious problem is the possible accidental gross contaminations which could affect Level 1 results. However, gross contamination is a problem associated with compliance by personnel with procedures and accepted techniques. The Q.A. technique discussed in Section A provides a method for limiting the risk of gross contamination on this basis.

To verify that continuous sampling of the same container is conservative, repeated sampling within containers is required. When it is demonstrated that the value of the blank remains sufficiently stable during the usage of the container that Level 1 accuracy will not be affected, sampling of that type of container can be limited.

B.2 Limiting Accuracy Required for Blank

Assume the Level 1 accuracy to be within a factor of 3 for sampling and analysis, and that the analysis alone is desired within a factor of 2. For a factor of 2, the ratio of the highest allowable value to the lowest is 4, i.e., $\frac{2\mu}{\mu/2} = 4$, where 2μ is the highest emission factor result and $\mu/2$ is the lowest, and μ is the true value. If the observed emission factor average (an estimate of μ) is A, then:

$$\frac{A + aA}{A - aA} = 4 \tag{A.1}$$

where a is the coefficient of variation divided by 100 times the multiple of the "t" distribution selected to express the expected variation.

When Equation (A.1) is solved, $a = 0.6$, hence the emission factor limiting accuracy is $A \pm 0.6A$.

A second consideration is that normal chemical practice does not permit values of blanks which constitute more than P percent of the total value, i.e., the blank X is not permitted if $X/(X + A) \times 100 > P$, where X is in emission factor units. Hence, the maximum error allowed for the blank (assuming no error in the uncorrected value) is:

$$|X - X_t| \leq (P/100)(0.6A) = 0.006PA \tag{A.2}$$

where X_t is the true value for the blank.

B.3 Cumulative Contamination of Solvent Blanks

Suppose a solvent container contains sufficient volume for m tests, and that a blank is always run on a new container. The first blank result in terms of emission factor units is X_o, and its error is $X_o - X_t$. The second blank error is then $X_1 - X_t$, and an estimate of the progressive contamination expected is $(X_1 - X_t) - (X_o - X_t) = X_1 - X_o = \Delta_1$.

Additional extimates of this progressive contamination are given by $(X_2 - X_1) = \Delta_2$, $(X_3 - X_2) = \Delta_3$, etc.

As long as the blanks are tested, the progressive error is accounted for, since the most recent blank is used in the computation and the residual error, $(X_i - X_t)$, becomes part of the overall reproducibility of the test, to be discussed in Section C. However, if blanks are no longer tested, the subsequent values for blanks must be approximated. One method for doing this is to determine the average change between consecutive blanks, $\overline{\Delta}$, and add one $\overline{\Delta}$ to each successive use, starting with the last measured value for the blank. $\overline{\Delta}$ is calculated from:

$$\left(\frac{1}{n-1}\right) \Sigma \, (X_{i+1} - X_i) = \overline{\Delta} = 1/(n-1) \, \Sigma \, \Delta_i \qquad \text{(A.3)}$$

If, for example, after n tests, no more blanks are run, the last result, X_n, will be used by adding to it $\overline{\Delta}$ for each succeeding use. There will be (m - n) times that the value for the blank will be used without further confirmation. The estimate to be used will be X_n, and $X_{n+1} = X_n + \overline{\Delta}$, $X_{n+2} = X_n + 2\overline{\Delta}$, and the last usage will be:

$$X_m = X_n + (m - n)\overline{\Delta}. \qquad \text{(A.4)}$$

If the last usage still meets the criteria of Level 1 accuracy, all earlier usages are also acceptable. The added variability of X_m is due to the uncertainty in knowing the value of $\overline{\Delta}$ to be used. This uncertainty is calculated from the standard deviation of $\overline{\Delta}$, which is:

$$S_{\overline{\Delta}} = \sqrt{\frac{\sum_{1}^{n} (\Delta_i - \overline{\Delta})^2}{(n-2)(n-1)}} \qquad \text{(A.5)}$$

The expected limit of variation of $\overline{\Delta}$ is taken as $tS_{\overline{\Delta}}$, where t is selected at a selected confidence level, and n - 2 degrees of freedom. Then, the estimated error of cumulated, but untested contamination of the blank is for X_m, $(m - n)\ tS_{\overline{\Delta}}$, and this is limited by Equation (A.2) to:

$$0.006PA \geq (m - n)\ tS_{\overline{\Delta}} \qquad (A.6)$$

or

$$\frac{S_{\overline{\Delta}}}{A} \leq \frac{0.006P}{(m - n)t} \qquad (A.7)$$

If $S_{\overline{\Delta}}/A$ is less than this limit, additional blank testing is not required. For example, suppose that we do not wish to make an excessively large blank correction more than one time in eight (12.5%). "Excessively large" is taken to mean that the blank is more than 10% of the emission factor (P = 10%), and the observed variation of the average blank already run is about ± 0.01A, 0.01A, expressed as the standard deviation, $S_{\overline{\Delta}}$, [Equation (A.5)]. Assume the container holds 10 usages, or m = 10. Then, from Equation (A.7):

$$\frac{0.006 \times 10}{(10 - n)t} \geq \frac{0.01A}{A}$$

$$6 \geq (10 - n)t$$

$$6/t \geq 10 - n.$$

By examination of the t table at n - 2 degrees of freedom (since we are using the variance of $\overline{\Delta}$, one degree of freedom is used to compute $\overline{\Delta}$).

n	t	10 - n	6/t
3	2.41	7	2.5
4	1.60	6	3.75
5	1.42	5	4.23
6	1.34	4	4.46
7	1.30	3	4.60

When 6 blanks have been tested, the blank correction can be calculated for the next 4.

Equation (A.7) was used to plot the cases where blanks are proposed to be tested for 1/3, 1/4, and 1/5 of the total usage of the reagent (n/m) for various sized containers. To do this, Equation (A.7) was modified to express the ratio n/m:

$$\frac{S_{\bar{\Delta}}}{A} = \frac{0.006P}{(m - n)t}$$

$$\frac{S_{\bar{\Delta}}}{A} = \frac{0.006P}{n(m/n - 1)t} \qquad (A.8)$$

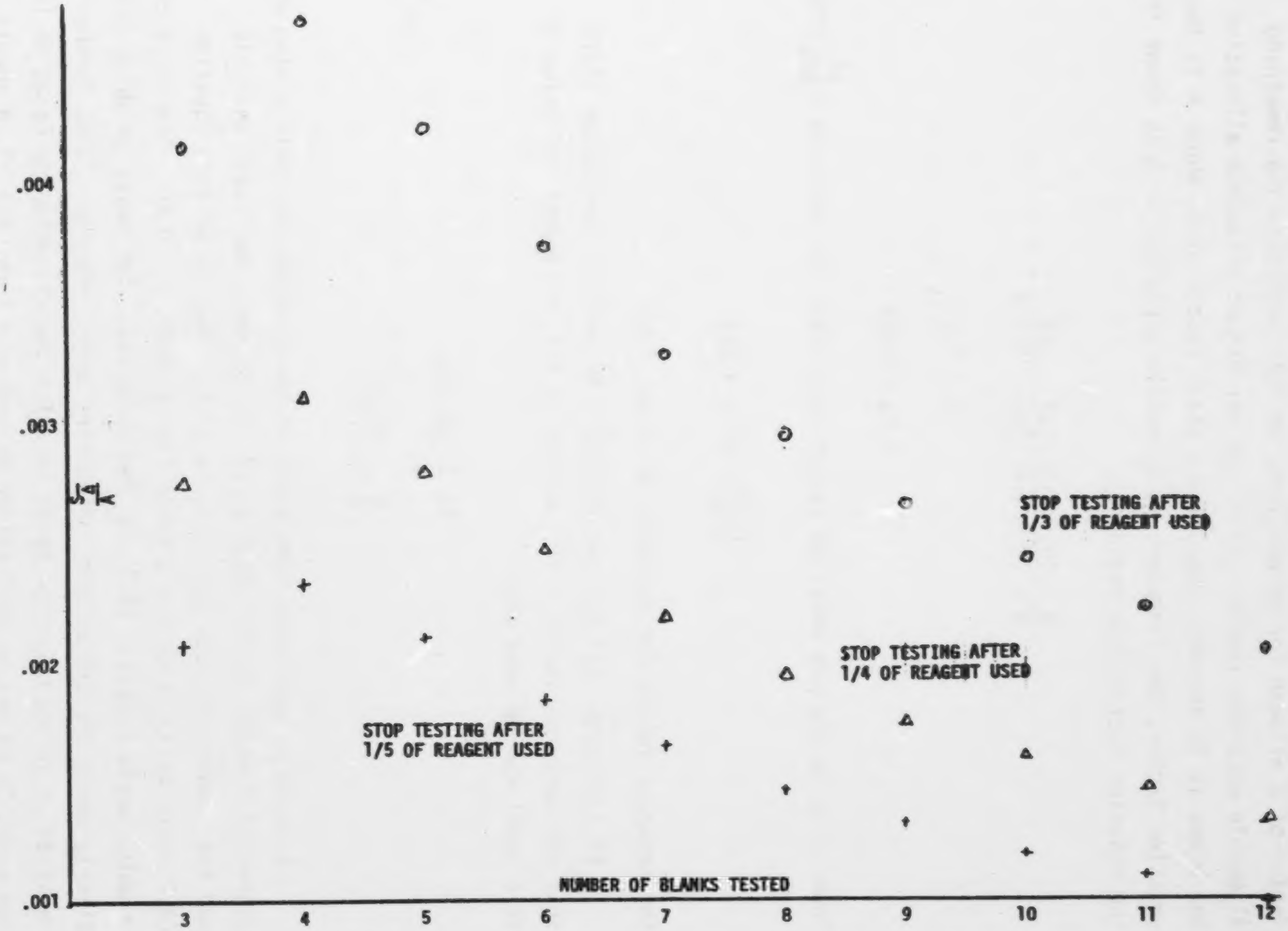
In the figure, the ratio $S_{\bar{\Delta}}/A$, the repeatability of the average difference between blanks to the emission factor value for a test (the ordinate) is a measure of the allowed lack of reproducibility of blanks for a given level of emission factor. Thus, when one-third of the total solvent usage times are tested for blanks, m/n = 3, only about half as accurate blanks are required than if only one-fifth of the total solvent usage times are tested, m/n = 5. Figure 1 shows:

- $S_{\bar{\Delta}}/A$ is initially stringent because the variability of the blank is not well-known.
- $S_{\bar{\Delta}}/A$ tends to become more stringent with containers which contain more total usages (increase in m), which is in the direction one would intuitively desire.
- An optimum reagent container size selection is possible.

C. SELECTION OF NUMBER OF REPLICATES FOR LEVEL 1 TESTING

In Section B, the accuracy factor, X, of 2 was used in finding the criteria for the repeating of a blank sample analysis. Since the

Figure 1. Minimum Repeatability Requirement for Discontinuance of Blank Tests



resulting blank sample testing limitations use up a part of the accuracy factor of 2 allowed for an analysis, we must determine the remaining allowable accuracy limits. If P, the percentage allowable allocation to the blank is 10 percent, then, for a total factor of 2, where A is the emission factor, the fraction, a, allowable variation in A is found from the emission factor data ratio, or:

$$\frac{A + (0.9 + 0.1)aA}{A - (0.9 + 0.1)aA} = \frac{2A}{1/2\ A} = 4$$

$$a = 0.6$$

$$0.9a = 0.54$$

Then, if x is the new emission factor data ratio for analysis $= \frac{xA}{A/x}$ and,

$$\frac{1.54}{0.46} = x^2 = 3.348$$

the accuracy factor for analysis is, thus, 1.83.

If replicate analyses should have a 90 percent confidence limit that the test results will fall within ±0.54A, a Student "t" value at this level can be used and,

$$tS \leqq \pm 0.54A \qquad \text{(A.9)}$$

$$\frac{S}{A} \leqq \frac{\pm 0.54}{t}$$

S is to be estimated from pairs of tests, with each pair giving one degree of freedom for S. Such a pair is called a duplicate analysis, and the numbers of such pairs, n, is to be found by solving Equation (A.9) with values from the t table (two-sided), $\beta = 0.10$. The value of n which meets Equation (A.9) is then selected. For tests in which S/A clearly meets the criteria by being very small, when n = 1, no further replication is needed. For tests in which the criteria for Equation (A.9) can probably be met by replication between n = 1 and n = 17, n should be selected from Equation (A.9) (n = 17 is a budget constraint that about 10 percent of the samples may be retested during the duration of the program). For tests which clearly will not meet the coefficient of variation, S/A, requirement [Equation (A.9)], the following method should be used.

The Level 1 accuracy requirement for these tests is 1.83 (see above). Even though σ, the true variation in the method, is too large to meet the accuracy requirement, it will be useful to limit the extent to which our test sample, S, can wander about the true value σ. If we know this, then we can at least identify the best accuracy factor that can be expected at a level of confidence.

We assume that the true value of the standard deviation, σ, should not be less than S/1.83, nor greater than 1.83S which is the accuracy factor ratio of 3.348 used before. This implies the only inaccuracy in the emission factor over σ is that due to our imperfect knowledge of σ, and hence is the best accuracy we could have.

Then, if we choose a 5 percent risk level for $0.547S < \sigma < 1.83S$, the sample size can be derived from an F table with (∞, n) degrees of freedom or directly from the table given in Dixon and Massey, Introduction to Statistical Analysis, 3rd Ed., McGraw-Hill, 1969, Pg. 469.

The lower limit, with only 5 percent chance of σ being smaller, can be established with $n = 2$. The upper limit with 95 percent chance that σ is not larger, can be established with $n = 6$.

Hence 6 replicates will adequately characterize σ at Level 1 accuracy under the assumptions made.

Equation (A.9) and the limit for S discussed above were used in Figure 2-10 as the decision criteria to discontinue replicate testing.

The decision plan of 2.6.5 was developed, however, as an extension of this approach to cover testing in more than one site, in which the same analytical method and technicians were used, and the general site complexities were the same. It is assumed that the sampling and analysis reproducibility is the same among these similar sites, and thus the variability obtained from the replicate analyses among the sites can be pooled and used to reduce the need for added replication. In this case, S, as used above becomes S_A (a pooled estimate of variability among the sites for analyses "A"), and the criteria uses A, which is the weighted average value of analyses "A" among the similar sites.

APPENDIX B

ANALYTICAL TRAVELER WORKSHEETS

Requestor ____________
JN ____________
Assigned to ____________
Date Assigned ____________

WORKSHEET FOR SOXHLET EXTRACTIONS - PROCEDURE 7.3.2

Summary: Samples are extracted for 24 hours with methylene chloride. At the end of the extraction, solvent sample is dried with sodium sulfate and concentrated with the Kuderna-Danish apparatus.

Sample Control Number (SCN)	Soxhlet Size	Sample Weight (g)	Aliquot Factor	Initial Solvent Volume (ml)	Completion Date/Initials	Comments and Observations

Requestor ____________________
JN ____________________
Assigned to ____________________
Date Assigned ____________________

WORKSHEET FOR KUDERNA-DANISH CONCENTRATIONS - PROCEDURE 7.4

Summary: The volume of each sample is measured and then each sample is dried and concentrated to ~ 5 ml. The concentrate is transferred to a 10 ml volumetric flask and brought to volume with the same solvent as the sample. Two 1 ml aliquots are taken for the GC and grav. analyses and the remaining 8 ml are transferred to a vial. All samples are labeled and placed in the refrigerator for storage.

Sample Control Number (SCN)	Sample Solvent	Sample Volume (ml)	Completion Date/Initials	Comments and Observations	Disbursement

Requestor ____________________

JN ____________________

Assigned to ____________________

Date Assigned ____________________

WORKSHEET FOR GRAVIMETRY – PROCEDURE 7.5

Summary: Each sample is received in a small glass bottle. The entire contents of each bottle are transferred to a tared aluminum weighing dish. The sample is allowed to evaporate to dryness at ambient conditions and is weighed back. IR scans are then conducted with the evaporated residues.

Sample Control Number (SCN)	Sample Solvent	Sample Aliquot Factor	Gravimetry, (g)	Grav. Completion Date/ Initials	IR Completion Date/ Initials	Comments and Observations
			Rsd & dish Dish ____________ Residue			
			Rsd & dish Dish ____________ Residue			
			Rsd & dish Dish ____________ Residue			
			Rsd & dish Dish ____________ Residue			
			Rsd & dish Dish ____________ Residue			
			Rsd & dish Dish ____________ Residue			
			Rsd & dish Dish ____________ Residue			
			Rsd & dish Dish ____________ Residue			
			Rsd & dish Dish ____________ Residue			

Requestor ______________

JN ______________

Assigned to ______________

Date Assigned ______________

WORKSHEET FOR GRAV/IR ON LC FRACTIONS - PROCEDURES 7.5 AND 7.6

Summary: Samples will usually be received in 10 or 25 ml volumetric flasks. The entire volume of each sample fraction is evaporated and weighed. Fractions 1 - 7 are done in aluminum pans and Fraction 8 in a small glass dish. If the grav. result is >15 mg, be careful to use no more than half the residue for the IR scan.

Sample Control Number (SCN)	Sample Volume (ml)	Sample Aliquot Factor	Gravimetry, (g)	Grav. Completion Date/ Initials	IR Completion Date/ Initials	Comments and Observations
Fraction 1			Rsd & dish Dish ______ Residue			
Fraction 2			Rsd & dish Dish ______ Residue			
Fraction 3			Rsd & dish Dish ______ Residue			
Fraction 4			Rsd & dish Dish ______ Residue			
Fraction 5			Rsd & dish Dish ______ Residue			
Fraction 6			Rsd & dish Dish ______ Residue			
Fraction 7			Rsd & dish Dish ______ Residue			
Fraction 8			Rsd & dish Dish ______ Residue			

Requestor ______________________
JN ______________________
Assigned to ______________________
Date Assigned ______________________

WORKSHEET FOR TCO (C7-C16) GC - PROCEDURE 7.7

Summary: Samples are received in small glass vials and are analyzed by the conditions and parameters set forth in the procedures manual. These parameters should also be recorded on the chromatogram. After analysis, the samples are stored in the refrigerator for subsequent POM GC/MS analysis.

Sample Control Number (SCN)	Comple-tion Date /Initials	Injection Volume, µl	Total Sample Volume, ml	Quantitation, µg											
				C7	C8	C9	C10	C11	C12	C13	C14	C15	C16	Total	

Requestor ______________
JN ______________
Assigned to ______________
Date Assigned ______________

WORKSHEET FOR LC SEPARATIONS - PROCEDURE 7.8

Summary: The indicated volume of sample is evaporated to a residue unless a solvent exchange is called for. The sample is then placed on the prepared column and eluted using 8 solvent fractions. The fractions are collected in volumentric flasks and 1 ml aliquots are taken if TCOs are to be done on the fractions, (i.e., those samples that go through the solvent exchange procedure).

Sample Control Number (SCN)	Solvent Exchange Needed	Sample Solvent	Aliquot To Be Taken (ml)	Organic Loading in LC Aliquot	Comments and Observations	Completion Date/ Initials

Requestor ____________________
JN ____________________
Assigned to ____________________
Date Assigned ____________________
Required Completion Date ____________________

WORKSHEET FOR POMs BY GC/MS - PROCEDURE 7.10

Summary: Generally 1 ml sample aliquots are received after their analysis for C7-17. The samples are then evaporated under a stream of high-purity inert gas and made up to 2 ml with the internal standard and benzene. Procedures for performing the GC/MS analysis are given in the EACCS manual and instrument operating manuals. Attach tabulation of reduced data to this worksheet.

Sample Control No. (SCN)	Sample Description	Type of Source	Initial Sample Volume (ml)	Volume Before Injection (ml)	Injection Volume (μl)	Date Complete/ Initials

Requestor ____________

Date Shipped ____________

Date Received ____________

Received By ____________

GC/MS PACKING SHEET

Complete, sign, and return to indicate receipt of samples.

Sample Control No. (SCN)	Volume	Sample Description	Condition After Shipment

DESICCATION OF SOLID SAMPLES TO CONSTANT WEIGHT

Completion Dates
1. ______ 2. ______
3. ______ 4. ______
Indicate by numbers in box under Sample column.

Requestor ______
JN ______
Assigned to ______
Date Assigned ______

ALL WEIGHTS IN GRAMS

TARE WEIGHT
1. ______
2. ______
3. ______
4. ______
5. ______
______
7. ______
8. ______
9. ______
10. ______
11. ______
12. ______
13. ______
14. ______
15. ______
16. ______

______ SAMPLE NUMBER
______ FILTER OR CONTAINER#
FILTER OR CONTAINER PLUS SAMPLE ______
FILTER OR CONTAINER TARE ______
SAMPLE ______

TARE + SAMPLE WEIGHT
1. ______
2. ______
3. ______
4. ______
5. ______
6. ______
7. ______
8. ______
9. ______
10. ______
11. ______
12. ______
13. ______
14. ______
15. ______
16. ______

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1. ______
2. ______
3. ______
4. ______
5. ______
6. ______
7. ______
8. ______
9. ______
10. ______
11. ______
12. ______
13. ______
14. ______
15. ______
16. ______

______ SAMPLE NUMBER
______ FILTER OR CONTAINER#
FILTER OR CONTAINER PLUS SAMPLE ______
FILTER OR CONTAINER TARE ______
SAMPLE ______

1. ______
2. ______
3. ______
4. ______
5. ______
6. ______
7. ______
8. ______
9. ______
10. ______
11. ______
12. ______
13. ______
14. ______
15. ______
16. ______

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1. ______
2. ______
3. ______
4. ______
5. ______
6. ______
7. ______
8. ______
9. ______
10. ______
11. ______
12. ______
13. ______
14. ______
15. ______
16. ______

______ SAMPLE NUMBER
______ FILTER OR CONTAINER#
FILTER OR CONTAINER PLUS SAMPLE ______
FILTER OR CONTAINER TARE ______
SAMPLE ______

1. ______
2. ______
3. ______
4. ______
5. ______
6. ______
7. ______
8. ______
9. ______
10. ______
11. ______
12. ______
13. ______
14. ______
15. ______
16. ______

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1. ______
2. ______
3. ______
4. ______
5. ______
6. ______
7. ______
8. ______
9. ______
10. ______
11. ______
12. ______
13. ______
14. ______
15. ______
16. ______

______ SAMPLE NUMBER
______ FILTER OR CONTAINER#
FILTER OR CONTAINER PLUS SAMPLE ______
FILTER OR CONTAINER TARE ______
SAMPLE ______

1. ______
2. ______
3. ______
4. ______
5. ______
6. ______
7. ______
8. ______
9. ______
10. ______
11. ______
12. ______
13. ______
14. ______
15. ______
16. ______

6-13

INORGANIC SAMPLE DISBURSEMENT WORKSHEET FOR SAMPLE COMBINATION

Completion Dates
1.______ 2.______
3.______ 4.______
Indicate by number in box under Sample column.

Requestor ____________
JN ____________
Assigned to ____________
Date Assigned ____________

SAMPLE COMBINATION DISBURSEMENT

1. Combine the indicated aliquots for each COMPOSITE sample into one plastic (liquids) or glass (solids) container. See Sec. 4.1.3.
2. Label the combined aliquots with the COMPOSITE SAMPLE NAME.

Quantities in grams or milliliters

COMPOSITE SAMPLE NAME	COMPOSITE TOTAL AMOUNT		COMBINE THESE SAMPLE ALIQUOTS TO MAKE COMPOSITE SAMPLE					
☐		SAMPLE #						
		AMOUNT						
☐		SAMPLE #						
		AMOUNT						
☐		SAMPLE #						
		AMOUNT						
☐		SAMPLE #						
		AMOUNT						
☐		SAMPLE #						
		AMOUNT						
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		AMOUNT						
☐		SAMPLE #						
		AMOUNT						

INORGANIC SAMPLE DISBURSEMENT WORKSHEET FOR SAMPLE PREPARATION

Completion Dates

1._______ 2. _______

3._______ 4. _______

Indicate by number in box under Sample column.

Requestor ________________

JN______________________

Assigned to________________

Date Assigned______________

SAMPLE PREPARATION DISBURSEMENT

1. Place the indicated (IND.) aliquot amounts for each sample into separate plastic (liquids) or glass (solids) containers.
   - A. Liquids – Use volumetric pipets or pipettors.
   - B. Solids – Cone and quarter to desired amount. Use microbalance. See Sec. 4.1.3.2 and Appendix D.
   - C. Filters – All filter weights are gross weights (filter + particulate). Use a pre-cleaned knife. See Sec. 4.1.3.3.
   - D. Slurries – Separate solids and liquids with Whatman #41 filter and Buchner funnel. Apportion solids and liquids as above.
2. Label these aliquotcontainers with: A. The sample name and B. The sample preparation, e.g., AR, etc.
3. Write the actual (ACT.) amount disbursed. Notify the requestor if IND. and ACT. differ by more than 5%.

Quantities in grams or milliliters

SAMPLE CONTROL NUMBER (SCN)		ORIGINAL AMOUNT	ALIQUOT FOR		ALIQUOT FOR		ALIQUOT FOR		ALIQUOT FOR		ALIQUOT FOR	
			IND	ACT	IND	ACT	IND	ACT	IND	ACT	IND	ACT

Completion Dates
1.______ 2.______
3.______ 4.______
Indicate by number in box under Sample column.

INORGANIC SAMPLE DISBURSEMENT WORKSHEET FOR SAMPLE ANALYSIS

Requestor ______________
JN ______________
Assigned to ______________
Date Assigned ______________

SAMPLE ANALYSIS DISBURSEMENT

1. Place the indicated (IND.) aliquot amounts for each sample into separate plastic (liquids) or glass (solids) containers.
   - A. Liquids – Use volumetric pipets or pipettors
   - B. Solids – Weighed on microbalance
   - C. Filters – Use a pre-cleaned knife
2. Label these aliquot containers with: A. The sample name and B. The sample analysis, e.g., Hg, AA, ICP, SSMS, etc.
3. Write the actual (ACT.) amount disbursed. Notify the requestor if IND. and ACT. differ by more than 5%.

Quantities in grams or milliliters

SAMPLE CONTROL NUMBER (SCN)		ORIG AMT	ALIQUOT FOR		ALIQUOT FOR		ALIQUOT FOR		ALIQUOT FOR		ALIQUOT FOR		ALIQUOT FOR		ALIQUOT FOR		ALIQUOT FOR		ALIQUOT FOR		ALIQUOT FOR		ALIQUOT FOR	
			IND	ACT	IND	ACT	IND	ACT	IND	ACT	IND	ACT	IND	ACT	IND	ACT	IND	ACT	IND	ACT	IND	ACT	IND	ACT

Requestor ____________________

JN ____________________

Assigned to ____________________

Date Assigned ____________________

WORKSHEET FOR PARR BOMB COMBUSTIONS - PROCEDURE 8.2.1

Summary: Samples for SSMS analysis are prepared by combusting a one gram sample using the quartz cup and lid arrangement. The combustion solution is rinsed directly into a Nalgene bottle made up to 50 ml, and labeled. Samples for Hg, As, Sb, SO_4, Cl, and/or F are prepared by a standard combustion of 1 to 2 grams of sample followed by digestion on a hot plate and filtration of the solids. The filtrate is then made up to 100 ml and labeled.

Sample Control No. (SCN)	Amount to be Taken/ For (g)	Sample Weighings	Final Volume (ml)	Date Complete /Initials	Disbursement

Requestor ____________________

JN ____________________

Assigned to ____________________

Date Assigned ____________________

WORKSHEET FOR AQUA REGIA DIGESTIONS - PROCEDURE 8.2.2

Summary: The weighed sample is placed in a boiling flask and is refluxed with constant boiling aqua regia for six hours on a hot plate. The solution is filtered into a Nalgene volumetric and made to a 100 ml volume when cool.

Sample Control No. (SCN)	Weight of Sample (mg)	Sample Aliquot Factor	Volume of Acid Used (ml)	Final Volume (ml)	Date Complete /Initials	Disbursement

Requestor ______________________
JN ______________________
Assigned to ______________________
Date Assigned ______________________

WORKSHEET FOR HOT WATER EXTRACTIONS - PROCEDURE 8.2.3

Summary: The weighed sample is placed in a boiling flask and is refluxed with deionized water for 1/2 hour. The solution is then filtered and made up to 50 ml volume for analysis.

Sample Control No. (SCN)	Weight of Sample (mg)	Sample Aliquot Factor	Volume of Water Used (ml)	Final Volume (ml)	Date Complete /Initials	Disbursement

Requestor ____________________
Assigned to ____________________
Date Assigned ____________________

WORKSHEET FOR SSMS ANALYSIS – PROCEDURE 8.3

Summary: Typically, either 100 ml of an aqueous solution on 100 mg of a solid are used to prepare the graphite sample electrodes. These electrodes are ionized and the resulting mass spectra are recorded on photoplates. Procedures for performing the SSMS analysis are given in the EACCS manual and instrument operating manuals. Attach tabulation of reduced data to this worksheet. Amounts used in this worksheet may be either volume or weight, so units must be given for each sample.

Sample Control No. (SCN)	Amount of Prepared Sample Received	Amount of Prepared Sample Used	Initial Amount of Prepared Sample	Ratio of Prepared to Total Sample	Appropriate Blank to be Subtracted	Factor to be Applied to Blank	Sample Gas Volume (DSCM)	Date Complete

Requestor ______________________

Date Shipped ______________________

Date Received ______________________

Received By ______________________

SSMS PACKING SHEET

Complete, sign, and return to indicate receipt of samples.

Sample Control No. (SCN)	Volume or Weight	Sample Description	Condition After Shipment

Requestor ____________________

JN ____________________

Assigned to ____________________

Date Assigned ____________________

WORKSHEET FOR COLD VAPOR MERCURY - PROCEDURE 8.4

Summary: **The indicated volume of sample is reduced with stannous chloride and the elemental mercury formed is sparged into a quartz cell where its absorbance at 253.7 nm is measured. Special procedures must be followed for different types of samples in order to get good results. The amount of Mercury in the sample aliquot is read from a calibration curve.**

Sample Control No. (SCN)	Type of Sample	Maximum Volume to be Taken (ml)	Actual Volume Taken (ml)	Sample Reading	Blank Reading	Mercury		Date Complete/ Initials
						Amount in Aliquot (μg)	Concentration ($\mu g/ml$)	

Requestor ____________________
JN ____________________
Assigned to ____________________
Date Assigned ____________________

WORKSHEET FOR ARSENIC HYDRIDE GENERATION – PROCEDURE 8.5

Summary: The indicated volume of sample is diluted, if necessary, to 25 ml and is reacted with zinc slurry and stannous chloride. The arsenic hydride formed is sparged into an argon–hydrogen flame in the AA with a stream of argon, and its concentration is measured at 193.7 nm. Special procedures must be followed for different types of samples in order to get good results. The amount of Arsenic is read from a calibration curve.

Sample Control No. (SCN)	Type of Sample	Maximum Volume to be Taken (ml)	Actual Volume Taken (ml)	Sample Reading	Blank Reading	Arsenic		Date Complete/Initials
						Amount in Aliquot (μg)	Concentration (μg/ml)	

Requestor ______________________

JN ______________________

Assigned to ______________________

Date Assigned ______________________

WORKSHEET FOR ANTIMONY HYDRIDE GENERATION - PROCEDURE 8.6

Summary: The indicated volume of sample is oxidized with H_2SO_4 and HNO_3, and then reacted with HCl, KI, and $SnCl_2$ reagents. The final hydride evolution is done with $NaBH_4$ and the antimony is sparged with nitrogen into a hydrogen diffusion flame in the AA. Its concentration is measured at 217.6 nm, and the amount of Antimony is read from a calibration curve.

Sample Control No. (SCN)	Type of Sample	Maximum Volume to be Taken (ml)	Actual Volume Taken (ml)	Sample Reading	Blank Reading	Antimony		Date Complete/ Initials
						Amount in Aliquot (μg)	Concentration (μg/ml)	

Requestor ____________________
JN ____________________
Assigned to ____________________
Date Assigned ____________________

WORKSHEET FOR TURBIDIMETRIC SULFUR – PROCEDURE 8.7

Summary: The indicated volume of sample is diluted, if necessary, to 100 ml, reacted with barium chloride, and its turbidity measured after 10 minutes. Colored and naturally turbid samples must also be measured before the addition of $BaCl_2$ reagent to obtain a blank reading.

Sample Control No. (SCN)	Maximum Volume to be Taken (ml)	Actual Volume Taken (ml)	Blank Reading For Color	Reacted Sample Reading	Sample Reading Minus Blank	SO_4		Date Complete/ Initials
						Amount in Aliquot (mg)	Concentration (mg/ml)	

Requestor ____________________
JN ____________________
Assigned to ____________________
Date Assigned ____________________

WORKSHEET FOR BRUCINE NITRATE - PROCEDURE 8.8

Summary: The indicated volume of sample is mixed with H_2SO_4 and brucine reagents under carefully temperature-controlled conditions. The developed color is measured at 410 mμ. Measurements are also made before the brucine reagent addition to correct for color already present in the sample by obtaining a blank reading.

Sample Control No. (SCN)	Maximum Volume to be Taken (ml)	Actual Volume Taken (ml)	Blank Reading For Color	Reacted Sample Reading	Sample Reading Minus Blank	NO_3		Date Complete/ Initials
						Amount in Aliquot (mg)	Concentration (mg/ml)	

Requestor ______________________

JN ______________________

Assigned to ______________________

Date Assigned ______________________

WORKSHEET FOR FLUORIDE ELECTRODE - PROCEDURE 8.9

Summary: The indicated volume of sample is diluted, if necessary, to 50 ml and the fluoride concentration is measured by specific ion electrode using a known additions technique.

Sample Control No. (SCN)	Type of Sample	Maximum Volume to be Taken (ml)	Actual Volume Taken (nl)	Dilution Factor	Initial Reading	Reading with Std. Addition	Fluoride Concentration in Undiluted Sample	Date Complete Initials

Requestor ____________________

JN ____________________

Assigned to ____________________

Date Assigned ____________________

WORKSHEET FOR CHLORIDE ELECTRODE – PROCEDURE 8.10

Summary: The indicated volume of sample is diluted, if necessary, to 100 ml and the chloride concentration is measured by specific ion electrode using a known additions technique.

Sample Control No. (SCN)	Type of Sample	Maximum Volume to be Taken (ml)	Actual Volume Taken (ml)	Dilution Factor	Initial Reading	Reading with Std. Addition	Chloride Concentration in Undiluted Sample	Date Complete/ Initials

Requestor ____________________
JN ____________________
Assigned To ____________________
Date Assigned ____________________

WORKSHEET FOR ____________________ DETERMINATION
BY ATOMIC ABSORPTION SPECTROSCOPY

Method (M): A = Flame AAS; B = Graphite Furnace AAS

A - FLAME PARAMETERS: Instrument ____________ Recorder ____________ mV ____________
Abs Line ______ nm Energy ______ Slit ______ Lamp Curr. ______ ma Fuel ______ Flow ______
Non Abs Line ______ nm Energy ______ Slit ______ Lamp Curr. ______ ma Oxidant ______ Flow ______

B - GRAPHITE FURNACE PARAMETERS: Instrument ____________ Argon Flow ____________ Ramp ____________
Abs Line ______ nm Energy ______ Slit ______ Lamp Curr. ______ ma DRY ______ sec. ______ amp ______ °C
Non Abs Line ______ nm Energy ______ Slit ______ Lamp Curr. ______ ma ASH ______ sec. ______ amp ______ °C
Complexing Reagents (CR): C = ______ μℓ D = ______ μℓ ATOM ______ sec. ______ amp. ______ °C
Empty Tube Readings (Noise) ____________________
Average Empty Tube Readings ____________ Detection Limit (2 x Noise) ____________

Sample Control Number (SCN)	M	CR	STD ADD	Maximum Volume Allowed	Dilution of Aliquot	Chart Reading	Minus Empty Tube	Concentration Aliquot	Slope	Correlation Coefficient

APPENDIX C

STANDARD EPA GAS SAMPLING METHODS

ENVIRONMENTAL PROTECTION AGENCY

[40 CFR Part 60]

[FRL 536-4]

STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES

Proposed Amendments to Reference Methods

On December 23, 1971, the Environmental Protection Agency promulgated standards of performance for five categories of stationary sources under section 111 of the Clean Air Act, as amended. An appendix to the regulation contained Reference Methods 1–9, which detailed requirements for performance testing of stationary sources. Since promulgation of these reference methods EPA has continued to evaluate them. As a result, the need for a number of changes which would clarify the methods and/or improve their accuracy and reliability has become apparent. The following proposed amendments incorporate these changes to Reference Methods 1–8. Revisions to Reference Method 9 were promulgated on November 12, 1974 (39 FR 39872).

Changes common to all eight of the reference methods are: (1) the clarification of procedures and equipment specifications, and (2) the addition of metric units along with English units. Specific changes to the methods are:

METHOD 1

A statement was added to clarify that the method does not apply to stacks containing cyclonic or swirling flow or stacks smaller than 0.3 m (1 ft) in diameter or 0.07 m^2 (0.8 ft^2) in cross sectional area. A procedure for verifying the existence of non-cyclonic or non-swirling flow was added. For cases where large cross sectional variation of the pollutant concentration is suspected or for unusually large diameter stacks, the method was revised to provide that more than two traverse diameters may be specified by the Administrator.

METHOD 2

The use of the method has been limited to non-cyclonic or non-swirling gas streams. Greater details for calibration of the Type S pitot tube have been added including: criteria for standard type pitot tubes; specification of calibration at 915 m/min (3000 ft/min); details of acceptable wind tunnel systems; and additional details for calibrating isolated pitot tubes and pitobe assemblies.

METHOD 3

For determining the molecular weight of a stack gas sample, it is now acceptable to use either an Orsat analyzer or a Fyrite[1] type combustion analyzer. Previously, only the Orsat analyzer was specified. The integrated gas-sampling train for this method was altered to include a surge tank before the rate meter in order to eliminate pulsation effects caused by the diaphragm pump. Also, because this method requires proportional sampling, an inclined manometer was added to the train to measure velocity head.

Where low CO$_2$ (less than 4%) or high O$_2$ (greater than 15%) concentrations exist, the procedure has been revised to require an Orsat having at least 0.1% subdivisions. The revised method also provides sampling site selection criteria and criteria for determining the number of sample points. More detail has been added to the analytical procedure. Finally, the former criteria for three consecutive measurements have been changed to require three measurements within 0.3% for greater than 3% CO$_2$ and 0.2% for less than 3% CO$_2$.

METHOD 4

This method now contains two separate methods for moisture determination: (1) a reference method for cases where the Method 5 train is not used, and (2) an approximation method for moisture content to be used for setting isokinetic sampling rates. In the moisture sampling train by the approximation method, the rate meter is now located before the dry gas meter.

METHOD 5

The specification for temperatures around the filter holder was revised to read "no greater than 120±14° C (248±25° F), or such other temperature as specified by an applicable subpart of the standards." The revised wording of the temperature specification does not change the procedure contained in the original method; it only clarifies the intended procedure by providing more specific instruction. The revised language also provides flexibility for the Administrator to specify other temperature limits in applicable subparts of the standards. Method 5 employs an out-of stack filter to facilitate temperature control. This usage is not changed by these proposed amendments. Specifications for weight and volume measurements were changed to reflect the capabilities of most widely used apparatus. To further insure the validity of the sample, leak checks of the sampling train are now required after sampling runs as well as before. Finally, the gas-sampling train was altered to include a stack gas temperature sensor.

METHOD 6

In the sampling train, the flow control valve is now located before the pump instead of after to allow better leak checks. Samples collected by the train are to be diluted to 100 ml instead of 50 ml to allow the number of rinses of the impingers necessary for adequate sample recovery. The average flow rate through the sampling train was reduced to 1 liter/min to prevent reagent carry-over from one impinger to the next.

METHOD 7

A provision was added to require the potassium nitrate used for preparation of the standard solution to be dried at 105–110° C for a minimum of two hours. Currently, during sample recovery, sodium hydroxide is added to the sample solution. These revisions require that only enough sodium hydroxide be added to adjust the pH to 9–12. This will prevent a large excess of sodium hydroxide. Similarly, during the analysis procedure, only enough ammonium hydroxide may be added to the sample to raise the pH to 10. This requirement prevents possible differences in color intensity due to an excess of ammonium hydroxide. Also during sample analysis, only one-half of the sample is to be analyzed to avoid loss of the sample due to analytical error. Finally, two changes concerning the spectrophotometer were made: (1) for spectrophotometer calibration, an equation is provided to determine a factor that insures the best fit through the calibration points, and (2) the absorbance measurement is now to be made at 410 nm instead of 420 nm.

METHOD 8

During sample analysis a 10 ml aliquot of SO$_2$ sample is specified instead of 25 ml to reduce the amount of titrant required. A stack gas temperature sensor was added to the integrated gas-sampling train.

Finally, EPA is presently in the process of converting the units in its standards to the International System of Units (SI). In keeping with this policy, we will soon convert the equipment specifications and procedures of the reference methods to SI. We anticipate that in some situations it will be necessary, for practical application, to use a mixture of SI and metric units. We solicit any comments that will expedite and facilitate this transition.

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[1] Mention of trade names is not intended to constitute endorsement by EPA.

By this notice, the Administrator is inviting comments on the proposed revisions. Submittals should, wherever possible, be supported with data and/calculations.

Comments on the proposed revisions should be submitted, in triplicate, to the Emission Standards and Engineering Division, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, Attention: Mr. Don R. Goodwin. All comments post-marked no later than July 23, 1976 will be considered.

Copies of comments received will be available for public inspection during normal business hours at the Public Information Reference Unit (EPA Library), Room 2922, 401 M Street, SW., Washington, D.C.

This amendment is proposed under the authority of section 111 of the Clean Air Act, as amended (42 U.S.C. 1857c6).

Dated: May 27, 1976.

JOHN QUARLES,
Acting Administrator.

It is proposed to amend Part 60 of Chapter I of Title 40 of the Code of Federal Regulations by revising Methods 1 through 8 of Appendix A—Reference Methods as follows:

APPENDIX A—REFERENCE METHODS

METHOD 1—SAMPLE AND VELOCITY TRAVERSES FOR STATIONARY SOURCES

1. *Principle and Applicability.*

1.1 Principle. A sampling site and the number of traverse points are selected to aid in the extraction of a representative sample.

1.2 Applicability. This method is applicable to sampling of gas streams contained in ducts, stacks, or flues.

It is intended that all new sources consider the requirements of this method before construction of the affected facility. Should they be overlooked, some sites may not lend themselves to this method and temporary alterations to the stack or deviation from the standard procedure may be required. Such cases are subject to approval by the Administrator.

This method is not applicable to stacks containing cyclonic or swirling flow (see § 2.4) or stacks smaller than about 0.3 m (1 ft) in diameter or 0.07 m² (0.8 ft²) in cross sectional area. When these cases are encountered, an alternate procedure, subject to approval of the Administrator, is required.

2. *Procedure.*

2.1 Sampling site. Select a sampling site that is at least 8 stack or duct diameters downstream and 2 diameters upstream from any flow disturbance such as a bend, expansion, contraction, or visible flame. If impractical, select an alternate site that is at least 2 stack or duct diameters downstream and 0.5 diameter upstream from the flow disturbances. For a rectangular cross section, use an equivalent diameter calculated from the following equation to determine the respective distances:

$$D_e=\frac{2LW}{L+W} \quad \text{Equation 1-1}$$

where:

D_e = equivalent diameter

L = Length

W = Width

2.2 Minimum number of traverse points. When the 8 and 2 diameter criterion can be met, the minimum number of traverse points shall be 12 for stack diameters greater than 0.6m (24 in.) and 8 for stack diameters equal to or less than 0.6 m (24 in.).

When the 8 and 2 diameter criterion cannot be met, use Figure 1-1 to determine the minimum number of traverse points. To use this figure, first determine the distances from the chosen sampling location to the nearest upstream and downstream disturbances. Divide each distance by the diameter or equivalent diameter to determine the distance in terms of the number of duct diameters. Then, determine from Figure 1-1 the minimum number of traverse points that corresponds (1) to the number of duct diameters upstream and (2) to the number of diameters downstream. Select the higher of the two minimum numbers of traverse points, or a greater value, such that for circular stacks the number is a multiple of four, and for rectangular stacks, the number follows the criteria in section 2.3.2.

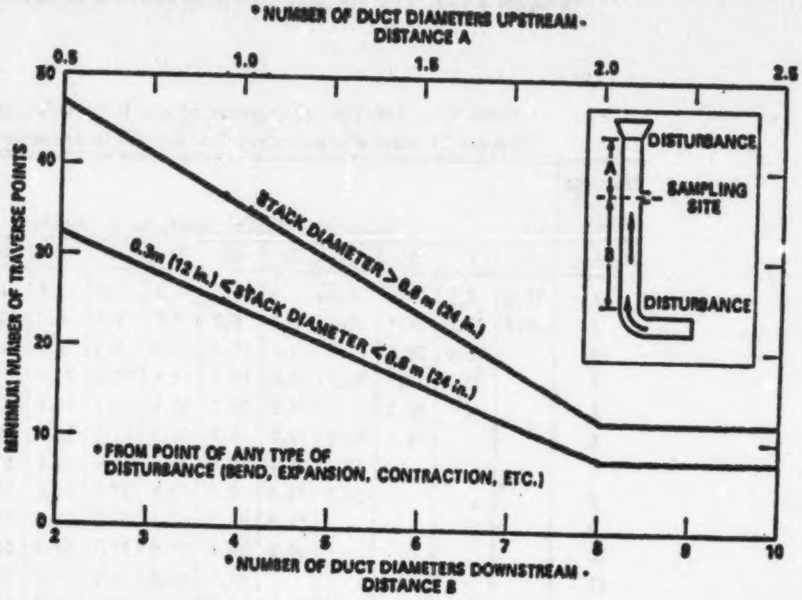

Figure 1-1. Minimum number of traverse points.

2.3 Cross sectional layout and location of traverse points.

2.3.1 Circular stacks. Locate the traverse points on two perpendicular diameters according to Table 1-1 and the example shown in Figure 1-2.

When large cross sectional variation of the pollutant concentration is suspected, the Administrator may specify that more than two diameters which divide the stack cross section into equal parts shall be used. More than two diameters may also be used with approval from the Administrator for unusually large diameter stacks.

One of the diameters shall be in a plane containing the greatest expected concentration variation, e.g., after bends one diameter shall be in the plane of the bend. This latter requirement becomes less critical as the distance from the disturbance increases. Therefore, other diameter locations may be used, subject to approval from the Administrator.

In addition, for stacks greater than 0.6 m (24 in.) no sampling points shall be selected within 2.54 cm (1 in.) of the stack walls, and for stacks equal to or less than 0.6 m (24 in.), no sampling points within 1.27 cm (½ in.) of the stack walls. To meet this criterion, do the following:

2.3.1.1 Stacks greater than 0.6 m (24 in.). When any of the traverse points, as located in section 2.3.1, fall within 2.54 cm (1 in.) of the stack walls, relocate them away from the stack walls to a distance of (1) 2.54 cm (1 in.) or (2) a distance equal to the nozzle inside diameter, whichever is larger. These relocated traverse points (on each end of a diameter) shall be the "adjusted" traverse points.

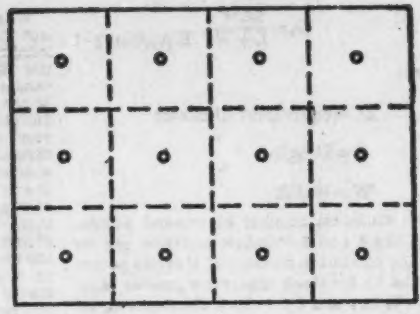

Figure 1-3. Example showing rectangular stack cross section divided into 12 equal areas, with traverse points at centroid of each area.

Table 1-1. Location of traverse points in circular stacks
(Percent of stack diameter from inside wall to traverse point)

Traverse point number on a diameter	Number of traverse points on a diameter											
	2	4	6	8	10	12	14	16	18	20	22	24
1	14.6	6.7	4.4	3.3	2.5	2.1	1.8	1.6	1.4	1.3	1.1	1.1
2	85.4	25.0	14.7	10.5	8.2	6.7	5.7	4.9	4.4	3.9	3.5	3.2
3		75.0	29.5	19.4	14.6	11.8	9.9	8.5	7.5	6.7	6.0	5.5
4		93.3	70.5	32.3	22.6	17.7	14.6	12.5	10.9	9.7	8.7	7.9
5			85.3	67.7	34.2	25.0	20.1	16.9	14.6	12.9	11.6	10.5
6			95.6	80.6	65.8	35.5	26.9	22.0	19.8	16.5	14.6	13.2
7				89.5	77.4	64.5	36.6	28.3	23.6	20.4	18.0	16.1
8				96.7	85.4	75.0	63.4	37.5	29.6	25.0	21.8	19.4
9					91.8	82.3	73.1	62.5	38.2	30.6	26.1	23.0
10					97.5	88.2	79.9	71.7	61.8	38.8	31.5	27.2
11						93.3	85.4	78.0	70.4	61.2	39.3	32.3
12						97.9	90.1	83.1	76.4	69.4	60.7	39.8
13							94.3	87.5	81.2	75.0	68.5	60.2
14							98.2	91.5	85.4	79.6	73.9	67.7
15								95.1	89.1	83.5	78.2	72.8
16								98.4	92.5	87.1	82.0	77.0
17									95.6	90.3	85.4	80.6
18									98.6	93.3	88.4	83.9
19										96.1	91.3	86.8
20										98.7	94.0	89.5
21											96.5	92.1
22											98.9	94.5
23												96.8
24												98.9

TRAVERSE POINT	DISTANCE, % of diameter
1	4.4
2	14.7
3	29.5
4	70.5
5	85.3
6	95.6

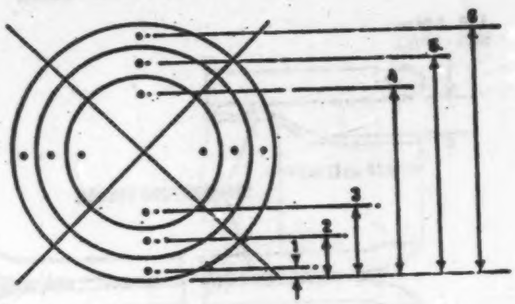

Figure 1-2. Example showing circular stack cross section divided into 12 equal areas, with location of traverse points at centroid of each area.

In some cases, two successive traverse points may need to be relocated to a single adjusted traverse point at each end of the traverse diameters. The sampling time at each of these "adjusted" traverse points shall be twice as long as at a "non-adjusted" sampling point as determined by the respective pollutant sampling method, e.g., Method 5.

2.3.1.2 Stacks equal to or less than 0.6 m (24 in.). Follow the procedure in section 2.3.1.1, noting only that the "adjusted" points should be relocated at 1.27 cm (0.5 in.) from the wall instead of 2.54 cm (1 in.).

2.3.2 Rectangular stacks. Divide the cross section into as many equal rectangular areas as traverse points as determined in sections 2.1 and 2.2 of this method, such that the ratio of the length to the width of the elemental areas is between one and two. Locate the traverse points at the centroid of each equal area according to the example in Figure 1–3.

The situation of section 2.3.1 concerning sampling points too close to the stack walls is not expected to arise with rectangular stacks. On the remote possibility that it does occur, consult with the Administrator.

2.4 Verification of non-cyclonic or non-swirling flow. Generally, cyclonic or swirling flow can be expected after such devices as cyclones and inertial demisters that follow venturi scrubbers or in stacks that have tangential inlets or two inlets that are opposite each other. At times, cyclonic flow can be detected by visual observations of the effluent plume. However, a Type S pitot tube as described in Method 2 can be used as a tool to verify the presence of cyclonic or swirling flow by doing the following:

2.4.1 Level and zero the manometer. Position the Type S pitot tube at each of the traverse points such that the face openings are perpendicular to the stack cross-sectional plane. A null (zero) reading at "0° reference" denotes the absence of cyclonic flow. If the reading is not zero, then rotate the pitot tube about ±10°. A null reading within the limits of ±10° rotation from 0° reference indicates an acceptable flow condition.

2.4.2 Conduct a velocity traverse according to Method 2. If there are negative velocity pressure readings, unacceptable flow conditions exist.

2.4.3 When unacceptable flow conditions are encountered, alternate procedures, subject to approval of the Administrator, are required.

3. *References.*

3.1 Determining Dust Concentration in a Gas Stream, ASME Performance Test Code #27, New York, N.Y., 1957.

3.2 Devorkin, Howard, et al., Air Pollution Source Testing Manual, Air Pollution Control District, Los Angeles, Calif., November 1963.

3.3 Methods for Determination of Velocity, Volume, Dust and Mist Content of Gases, Western Precipitation Division of Joy Manufacturing Co., Los Angeles, Calif. Bulletin WP-50, 1968.

3.4 Standard Method for Sampling Stacks for Particulate Matter, In: 1971 Book of ASTM Standards, Part 23, Philadelphia, Pa. 1971. ASTM Designation D-2928-71.

METHOD 2—DETERMINATION OF STACK GAS VELOCITY AND VOLUMETRIC FLOW RATE (TYPE S PITOT TUBE)

1. *Principle and Applicability.*

1.1 Principle. Stack gas velocity is determined from the gas density and from measurement of the velocity head using a Type S (Stausscheibe or reverse type) pitot tube.

1.2 Applicability. This method is applicable for measurement of the average velocity of a gas stream and for quantifying gas flow.

This procedure is not applicable for direct measurement in cyclonic or swirling gas streams. (Method 1, section 2.4 shows how to determine unacceptable flow conditions.) When these conditions exist, procedures such as the use of flow straightening devices must be employed subject to approval by the Administrator, to make accurate flow rate determinations.

2. *Apparatus.*

Specifications for the apparatus are given below. Any apparatus which has been demonstrated subject to approval of the Administrator, to be capable of meeting the specifications will be considered acceptable for the purposes of this method.

2.1 Pitot tube. Type S (Figure 2–1), or equivalent, calibrated according to the procedure in section 4. Other devices may be used when approved by the Administrator.

2.2 Differential pressure guage. Inclined manometer, or equivalent device, capable of measuring velocity head to within 10% of the minimum measured value or ±0.013 mm (0.005 in.), whichever is greater. Below a differential pressure of 1.3 mm (0.05 in.) water gauge, micromanometers with sensitivities of 0.013 mm (0.0005 in.) should be used. However, micromanometers may not easily be adaptable to the existing field conditions and are not easy to use with pulsating flow. Thus, alternative methods or other devices acceptable to the Administrator may be used when conditions warrant.

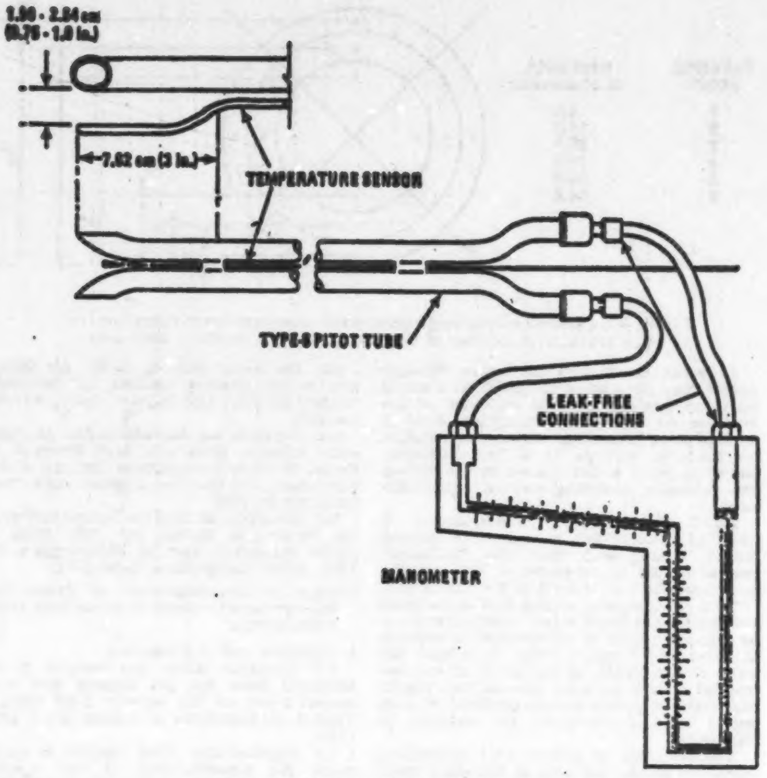

Figure 2-1. Pitot tube-manometer assembly.

The calibration of magnehelics, if used, must be checked on-site before and after each test run.

2.3 Temperature gauge. Thermocouple, liquid filled bulb thermometer, bimetallic the.mometer, mercury-in-glass thermometer, or other gauges that are capable of measuring temperature to within 1.5% of the minimum absolute stack temperature. The temperature gauge shall be attached to the pitot tube such that the sensor does not touch any metal and its position is adjacent and about 1.90 to 2.54 cm (0.75 to 1 in.) from the pitot tube openings (see Figure 2-1). Alternate positions may be used if the pitot tube-temperature gauge system is calibrated according to the procedure of section 4. If it can be shown to the satisfaction of the Administrator that a difference of not more than 1% in the velocity measurement will be introduced, the temperature gauge need not be attached to the pitot tube.

2.4 Pressure probe and gauge. Piezometer tube and mercury- or water-filled U-tube manometer capable of measuring stack pressure to within 2.5 mm Hg (0.1 in. Hg). The static tap of a standard type pitot tube or one leg of a Type S pitot tube with the face openings positioned parallel to the gas flow may also be used as the pressure probe.

2.5 Barometer. Mercury, aneroid, or other barometers capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby weather bureau station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and the sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.6 Gas analyzer. To analyze gas composition for determining molecular weight. Use Method 3 or other methods specified by the Administrator for dry molecular weight and use Method 5 or Reference Method 4 for moisture content. Other methods may be used when approved by the Administrator.

2.7 Calibration pitot tube. Standard type, to calibrate the Type S pitot tube. The standard type pitot tube shall have a known coefficient obtained from the National Bureau of Standards, Route 70 S, Quince Orchard Road, Gaithersburg, Maryland. An alternative is to use a Prandtl type pitot tube designed according to the criteria (given below and illustrated in Figure 2-2; see also Reference 6.7 or 6.8 for greater detail) which ensure that its coefficient will be 0.99±0.01.

2.7.1 Hemispherical or ellipsodial tip (inlet end of the impact tube).

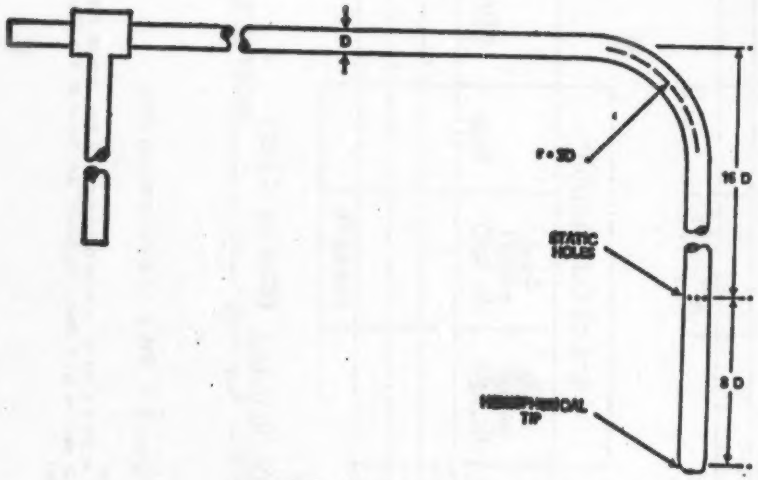

Figure 2-2. Standard Pitot tube.

2.7.2 Eight diameters of straight run (based on the diameter of the external tube) between the tip and the static pressure holes.

2.7.3 Sixteen diameters between the static pressure holes and the centerline of the external tube, following the 90° bend.

2.7.4 Eight static pressure holes of equal size (approximately 0.71 mm or 1/32 in. diameter), equally spaced in a piezometer ring configuration.

2.7.5 Ninety-degree bend of relatively large radius (approximately three diameters).

2.8 Calibration differential pressure gauge—For calibration purposes, inclined manometer, or equivalent device, capable of measuring velocity head to within 0.13 mm H_2O (0.005 in. H_2O).

3. *Procedure.*

3.1 Set up the apparatus as shown in Figure 2-1. Make sure all connections are tight and leak free. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the sample run. Record all necessary data as shown in the example data sheet (Figure 2-3).

3.2 Measure the velocity head and temperature at the traverse points specified by Method 1.

3.3 Measure the static pressure in the stack. One reading is usually adequate for all measuring points during the test; however, this must be confirmed by randomly moving the pressure probe over the cross section to see if there are any significant variations, i.e., greater than about 100 mm H_2O (4 in. H_2O). If there are significant variations, check the location for disturbances. If none are found, measure and record the static pressure at each traverse point.

PLANT ____________
DATE ____________ RUN NO. ____________
STACK DIAMETER OR DIMENSIONS, m(in.) ____________
BAROMETRIC PRESSURE, mm Hg (in. Hg) ____________
CROSS SECTIONAL AREA, m^2(ft^2) ____________
OPERATORS ____________
PITOT TUBE I.D. NO. ____________
AVG. COEFFICIENT, C_p = ____________
LAST DATE CALIBRATED ____________

SCHEMATIC OF STACK CROSS SECTION

Traverse Pt. No.	Vel. Hd., Δp mm (in.) H_2O	Stack Temperature		P_g* mm Hg (in. Hg)	$\sqrt{\Delta p}$
		t_s, °C (°F)	T_s, °K (°R)		
	Average				

*If preliminary investigation shows that P_g varies no more than 100 mm H_2O (4 in. H_2O), record one reading.

Figure 2-3. Velocity traverse data.

3.4 Determine the atmospheric pressure.

3.5 Determine the dry stack gas molecular weight. For combustion processes, use Method 3. For processes emitting essentially air, an analysis need not be conducted: use a molecular weight of 29. For other processes, consult the Administrator.

3.6 Obtain the moisture content from Method 5 or by using Preference Method 4.

3.7 Determine the cross sectional area of the stack or duct at the sampling location. Whenever possible, it is better to physically measure the stack dimensions rather than using blueprints.

4. *Calibration.*

4.1 Pitot tube.

4.1.1 Calibration set-up—Calibration shall be done in a flow system having the following essential design features:

4.1.1.1 The flowing gas stream must be confined to a definite cross-sectional area, either circular or rectangular. For circular cross-sections, the minimum duct diameter shall be 30.5 cm (12 inches); for rectangular cross-sections, the width (shorter side) shall be at least 25.4 cm (10 inches).

4.1.1.2 The cross sectional area must be constant over a distance of 10 or more duct diameters. For a rectangular cross section, use an equivalent diameter calculated from he following equation to determine the number of duct diameters:

$$D_e = \frac{2LW}{(L+W)} \quad \text{Equation 2-1}$$

where:

D_e = Equivalent diameter

L = Length

W = Width

To ensure the presence of stable, fully developed flow patterns at the calibration site, or "test section," the site must be located at least 8 diameters downstream and two diameters upstream from the nearest disturbances.

NOTE.—Wind tunnels with well-developed flow patterns (i.e., flow parallel to the duct axis) may also be used.

4.1.1.3 The flow system shall have the capacity to generate a test-section velocity around 915 m/min. (3000 ft/min.), which is the approximate midpoint of the "normal working range" 305 to 1525 m/min. or ~1000 to 5000 ft/min. This velocity must be constant with time, to guarantee steady flow during calibration.

Note that Type-S pitot tube coefficients obtained by single-velocity calibration at the midpoint of the normal working range will generally be valid to within ±3 percent over the entire range. If a more precise correlation between C_p and velocity is desired, the flow system shall have the capacity to generate a number of distinct, time-invariant test-section velocities, covering the normal working range, and calibration data shall be taken at regular velocity intervals between 305 and 1525 m/min. (1000 and 5000 ft/min.). (See Reference 6.9 for details.)

4.1.1.4 Two entry ports, one each for the standard and Type S pitot tubes, shall be cut in the test section; the standard pitot entry port shall be located slightly downstream of the Type S port, so that the standard and Type S impact openings will lie in the same cross-sectional plane during calibration. To facilitate alignment of the pitot tubes during calibration, it is adviseable that the test section be constructed of plexiglas or some other transparent material.

4.1.2 Calibration procedure. Note that this procedure is a general one, and must not be used without first referring to the specific considerations presented in sections 4.1.4–4.1.5. Note also that this procedure applies only to single-velocity calibration; see Preference 6.9 for more details. It is recommended that an identification number be assigned to the pitot tube, and that this number be permanently marked or engraved on the body of the tube; also, one leg of the tube should be marked "A", and the other, "B". To obtain calibration data for both the "A" and "B" sides, proceed as follows:

4.1.2.1 Make sure that the manometer is properly filled and that the oil is free from contamination. Inspect and leak-check all pitot lines; repair or replace if necessary.

4.1.2.2 Level and zero the manometer. Turn on the fan and allow the flow to stabilize. Seal the Type S entry port.

4.1.2.3 Ensure that the manometer is level and zeroed. Position the standard pitot tube at the calibration point (determined as outlined in sections 4.1.4 and 4.1.5), and align it so that its tip is pointed directly into the flow. Particular care should be taken in aligning the tube, to avoid yaw and pitch angles. Make sure that the entry port surrounding the tube is properly sealed.

4.1.2.4 Read ΔP_{std} and record its value in a data table, similar to the one shown in Figure 2-4. Remove the standard pitot tube from the duct and disconnect it from the manometer. Seal the standard entry port.

4.1.2.5 Connect the Type S pitot tube to the manometer. Open the Type S entry port. Check the manometer level and zero. Insert and align the Type S pitot tube so that its "A" side impact opening is at the same point as was the standard pitot tube, and is pointed directly into the flow. Make sure that the entry port surrounding the tube is properly sealed.

4.1.2.6 Read ΔP_s and enter its value in the data table. Remove the Type S pitot tube from the duct and disconnect it from the manometer.

4.1.2.7 Repeat steps 4.1.2.3 through 4.1.2.6 above, until three sets of velocity head readings have been obtained.

4.1.2.8 Repeat steps 4.1.2.3 through 4.1.2.7 above for the B-side of the Type S pitot tube.

PITOT TUBE IDENTIFICATION NUMBER:________ DATE:__________

CALIBRATED BY:______________________________

	"A" SIDE CALIBRATION			
RUN NO.	Δp_{std} cm H_2O (in. H_2O)	$\Delta p_{(s)}$ cm H_2O (in. H_2O)	$C_{p(S)}$	DEV.
1				
2				
3				
		AVERAGE		

	"B" SIDE CALIBRATION"			
RUN NO.	Δp_{std} cm H_2O (in. H_2O)	$\Delta p_{(s)}$ cm H_2O (in. H_2O)	$C_{p(S)}$	DEV.
1				
2				
3				
		AVERAGE		

DEV. = $\underline{C_{p(S)} - C_{p(S)(avg.)}}$ (MUST BE ≤ 0.01)

C_p DIFFERENCE: $A_{avg} - B_{avg}$ =____________(MUST BE ≤ 0.01)

Figure 2-4. Pitot tube calibration data.

4.1.3 Calculations.

4.1.3.1 For each of the 6 pairs of velocity head readings (i.e., 3 from Side A and 3 from side B) obtained in section 4.1.2 above, calculate the value of the Type S pitot tube coefficient, as follows:

$$C_{p(S)} = C_{p(std)} \sqrt{\frac{\Delta p_{std}}{\Delta p_S}} \qquad \text{Equation 2-2}$$

where:

$C_{p(S)}$=Type S pitot tube coefficient
$C_{p(std)}$=Standard pitot tube coefficient; use 0.99 if the coefficient is unknown and the tuele is designed according to the guidelines in section 2.7
Δp_{std}=Velocity head measured by the standard pitot tube, cm H_2O (in. H_2O)
Δp_S=Velocity head measured by the Type S pitot tube, cm H_2O (in. H_2O)

4.1.3.2 Calculate $\bar{C}_p$ (side A), the mean A-side coefficient, and $\bar{C}_p$ (side B), the mean B-side coefficient; calculate the difference between these two average values.

4.1.3.3 Calculate the deviation of each of the three A-side values of $C_{p(S)}$ from $\bar{C}_p$ (side A), and the deviation of each B-side value of $C_{p(S)}$ from $\bar{C}_p$ (side B). Use the following equation:

$$\text{Deviation} = C_{p(S)} - \bar{C}_p(\text{A or B}) \qquad \text{Equation 2-3}$$

4.1.3.4 Calculate σ, the average deviation from the mean, for both the A and B sides of the pitot tube. Use the following equation:

$$\sigma(\text{side A or B}) = \frac{\sum_{1}^{3} |C_{p(S)} - \bar{C}_p(\text{A or B})|}{3} \qquad \text{Equation 2-4}$$

4.1.4 Specific considerations pertaining to calibration of isolated type S pitot tubes. When an isolated Type S pitot tube is to be calibrated, select a calibration point at or near the center of the duct, and follow the procedures outlined in sections 4.1.2 and 4.1.3 above. The coefficients so obtained, i.e., $\bar{C}_p$ (side A) and $\bar{C}_p$ (side B), will be valid for the measurement of stack gas velocities between 305 and 1525 m/min. (1000 and 5000 ft/min.), so long as the isolated pitot tube is used. If, however, the pitot tube is used as a component of a pitobe assembly, the isolated coefficient values may or may not apply; this is discussed more fully in section 4.1.5.

4.1.5 Pitobe Assemblies. Generally, when a Type S pitot tube is used as a component of a pitobe assembly, its A and B-side coefficients will differ appreciably from their respective isolated values if there is aerodynamic interactions among the assembly components. The isolated and assembly coefficient values will only be the same if the assembly is constructed according to the following specifications:

(a) To minimize aerodynamic interactions between the pitot tube and sampling nozzle there must be a separation distance (free-space) of at least 1.90 cm (¾ in.) between the nozzle and pitot tube, with the largest size nozzle (usually 1.3 cm or ½ in., i.d.) in place. (See Figure 2–5.)

(b) To minimize aerodynamic interactions between the thermocouple and pitot tube, the thermocouple wire must be mounted on the pitot tube in such a way that the tip of the wire is in line with, but at least 1.90 cm (¾ in.) from the center of the pitot tube impact openings. (See Figure 2–6.)

(c) To eliminate pitot tube-probe sheath interference, there must be at least 7.62 cm (3 in.) between the leading edge of the probe and the center of the pitot tube impact openings. (See Figure 2–7.)

For those assemblies which either (1) meet requirements (a) through (c) above but have unknown isolated coefficients, or (2) fail to meet these requirements, use the procedures to calibrate the pitot tube-nozzle-thermocouple assemblies outlined in sections 4.1.2 and 4.1.3, in conjunction with the following special considerations, to determine the A and B-side coefficients of the Type S pitot tube:

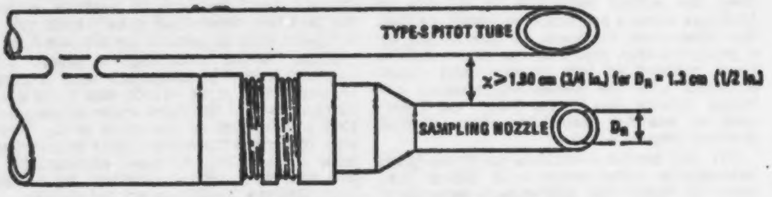

Figure 2-5. Minimum pitot-nozzle separation needed to prevent interference.

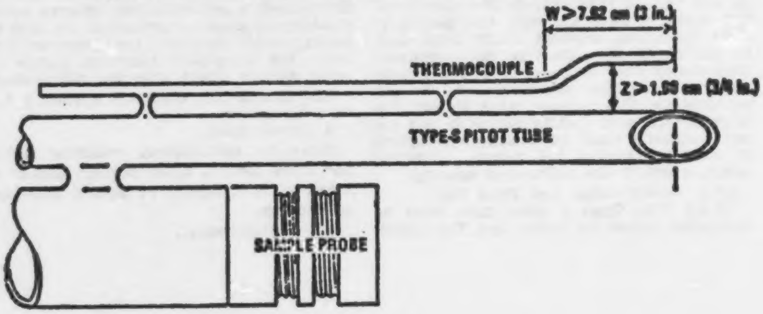

Figure 2-6. Proper thermocouple placement to prevent interference.

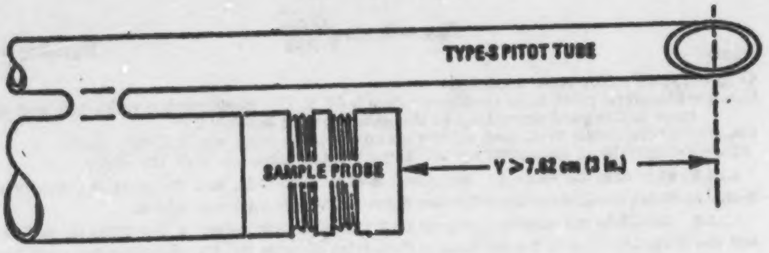

Figure 2-7. Minimum pitot-sample probe separation needed to prevent interference.

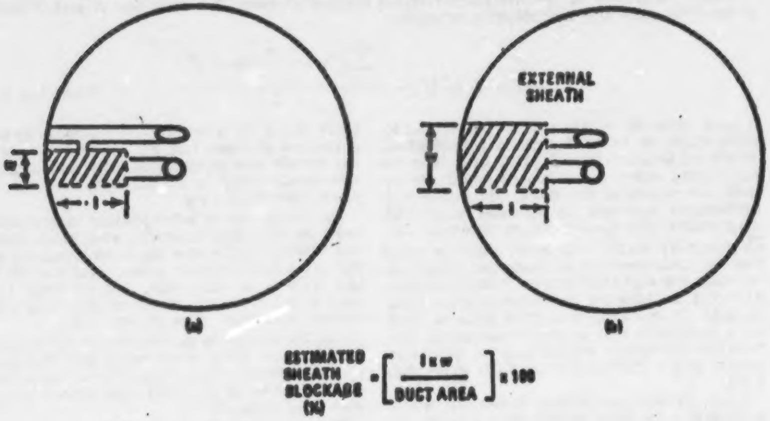

Figure 2-8. Projected-area models for typical pitobe assemblies.

(i) Although it is preferable that the calibration point be located at or near the center of the duct, insertion of a probe sheath into a small duct may cause significant cross-sectional area blockade, and yield incorrect coefficient values. Therefore, to minimize the blockage effect, the calibration point may be a few inches off-center if necessary. To keep the actual reduction in C_p due to blockage below 1 percent, it is necessary that the theoretical blockage, as determined by a projected-area model of the probe sheath, be 2 percent or less of the duct cross-sectional area for assemblies without external sheaths (see Figure 2-8a) and 3 percent or less for assemblies with external sheaths (Figure 2-8b).

(ii) For pitobe assemblies in which pitot tube-nozzle interference is a factor (i.e., those in which the pitot-nozzle separation distance is less than 1.90 cm (¾ in.) with a 1.3 cm (½ in.) nozzle in place) the value of C_p will depend somewhat on the amount of free space between the tube and nozzle; in these instances, separate calibrations shall be performed with each of the commonly used nozzle sizes in place. Note that single-velocity calibration technique will be acceptable for this purpose, even though the larger nozzle sizes (>0.635 cm or ¼ in.) are not ordinarily used for isokinetic sampling at velocities around 915 m/min. (3000 ft/min.), which is the calibration velocity.

4.1.6 Recalibration and Field Use.

4.1.6.1 The Type S pitot tube shall be calibrated before its initial use. Thereafter, if the tube has been significantly damaged by field use (for example, if the impact openings are bent out of shape, cut, nicked, or noticeably misaligned), it shall be repaired if possible and recalibrated, or replaced, if necessary.

4.1.6.2 When the Type S pitot tube is used in the field, the appropriate A or B-side coefficient shall be used to perform velocity calculations, depending upon which side of the pitot tube is pointed toward the flow.

4.1.6.3 When sampling a small duct (~12-36 inches in diameter) with a pitobe assembly, the probe sheath can block a significant part of the duct cross-section, causing a reduction in the value of C_p. Therefore, in certain instances it may be necessary, prior to sampling, to make adjustments in the coefficient values obtained by calibration. Consult Reference 6.9 for details.

4.2 Temperature gauges. Calibrate dial and liquid filled bulb thermometers and thermocouple-potentiometer systems against mercury-in-glass thermometers. Ice bath and boiling water (corrected for barometric pressure) are acceptable reference points. For other devices, check with the Administator.

4.3 Barometers. Calibrate against a mercury barometer.

5. *Calculations.*

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

5.1 Nomenclature.

A = Cross sectional area of stack, m^2 (ft^2)
B_{ws} = Water vapor in the gas stream (from Method 5 or Reference Method 4), proportion by volume
C_p = Pitot tube coefficient, dimensionless
K_p = Pitot tube constant,

$$34.97\ \frac{m}{sec}\left[\frac{(g/g\text{-mole})(mm\ Hg)}{(°K)(mm\ H_2O)}\right]^{1/2}$$

for the metric system and

$$85.48\ \frac{ft}{sec}\left[\frac{(lb/lb\text{-mole})(in.\ Hg)}{(°R)(in.\ H_2O)}\right]^{1/2}$$

for the English system
M_d = Molecular weight of stack gas, dry basis (from Method 3 or other approved methods), g/g-mole (lb/lb-mole)
M_s = Molecular weight of stack gas, wet basis, g/g-mole (lb/lb-mole)
$= M_d(1-B_{ws})+18B_{ws}$ Equation 2-5
P_{bar} = Atmospheric pressure, mm Hg (in. Hg)
P_g = Stack static pressure, mm Hg (in. Hg)
P_s = Absolute stack gas pressure, mm Hg (in. Hg)
$= P_{bar}+P_g$ Equation 2-6
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg)
Q_{sd} = Dry volumetric stack gas flow rate corrected to standard conditions, dscm/hr (dscf/hr)
t_s = Stack temperature, °C (°F)
T_s = Absolute stack temperature, °K (°R)
$= 273+t_s$ for metric Equation 2-7
$= 460+t_s$ for English Equation 2-8
T_{std} = Standard absolute temperature, 293°K (528°R)
v_s = Average stack gas velocity, m/sec (ft/sec)
Δ_p = Velocity head of stack gas, mm H_2O (in. H_2O)
3600 = Conversion factor, sec/hr
18 = Molecular weight of water, g/g-mole (lb/lb-mole)

5.2 Average stack gas velocity.

$$v_s = K_pC_p(\sqrt{\Delta p})_{avg}\sqrt{\frac{(T_s)_{avg}}{P_sM_s}} \qquad \text{Equation 2-9}$$

NOTE.—Equation 2-7 assumes that T_s, P_s, and M_s do not change appreciably (i.e. $>1\%$) with cross section and with time. If they do, consult with the Administrator to determine an acceptable procedure.

5.3 Average stack gas dry volumetric flow rate.

$$Q_{sd} = 3600(1-B_{ws})V_sA\left[\frac{T_{std}}{T_{s(avg)}}\right]\left[\frac{P_s}{P_{std}}\right] \qquad \text{Equation 2-10}$$

6. *References.*

6.1 Mark, L. S., Mechanical Engineer's Handbook, McGraw-Hill Book Co., Inc., New York, N.Y. 1951.

6.2 Perry, J. H., Chemical Engineers' Handbook, McGraw-Hill Book Co., Inc., New York, N.Y., 1960.

6.3 Shigehara, R. T., W. F. Todd, and W. S. Smith, Significance of Errors in Stack Sampling Measurements. Paper presented at the Annual Meeting of the Air Pollution Control Association, St. Louis, Mo., June 14-19, 1970.

6.4 Standard Method for Sampling Stacks for Particulate Matter. In: 1971 Book of ASTM Standards, Part 23, Philadelphia, Pa., 1971. ASTM Designation D-2928-71.

6.5 Vennard, J. K., Elementary Fluid Mechanics, John Wiley & Sons, Inc., New York, N.Y., 1947.

6.6 ASME, Fluid Meters—Their Theory and Application, ASME, N.Y., 1959.

6.7 ASHRAE Handbook of Fundamentals, 1972, p. 208.

6.8 ASTM Annual Book of ASTM Standards, Part 26, 1974, p. 648.

6.9 Vollaro, R. F., Guidelines for Type-S Pitot Tube Calibration. Paper presented at 1st Annual Meeting, Source Evaluation Society, Dayton, Ohio; September 18, 1975.

METHOD 3—GAS ANALYSIS FOR CARBON DIOXIDE, OXYGEN, EXCESS AIR, AND DRY MOLECULAR WEIGHT

1. *Principle and Applicability.*

1.1 Principle. An integrated or grab gas sample is extracted from a stack and analysed for percent carbon dioxide and percent oxygen using an Orsat analyser or, for molecular weight determinations, a *Fyrite*[1] type combustion gas analyser.

1.2 Applicability. This method is applicable for determining carbon dioxide and oxygen concentrations, and molecular weight of a sample from a gas stream.

2. *Apparatus.*

Any apparatus which has been demonstrated to yield results acceptable to the Administrator will be considered acceptable for the purposes of this method.

2.1 Grab sample (Figure 3-1).

2.1.1 Probe—Stainless steel or borosilicate glass equipped with a filter (either in-stack or out-stack) to remove particulate matter.

2.1.2 Pump—One-way squeeze bulb, or equivalent, to transport gas sample to analyser.

2.2 Integrated sample (Figure 3-2).

2.2.1 Probe—Stainless steel or borosilicate glass equipped with a filter (either in-stack or out-stack) to remove particulate matter.

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[1] Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

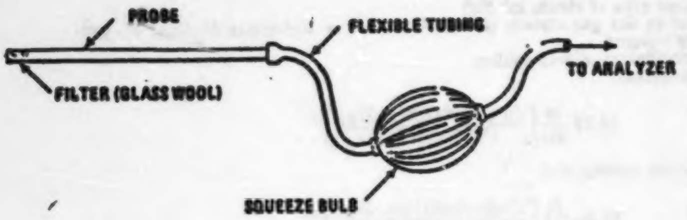

Figure 3-1. Grab-sampling train.

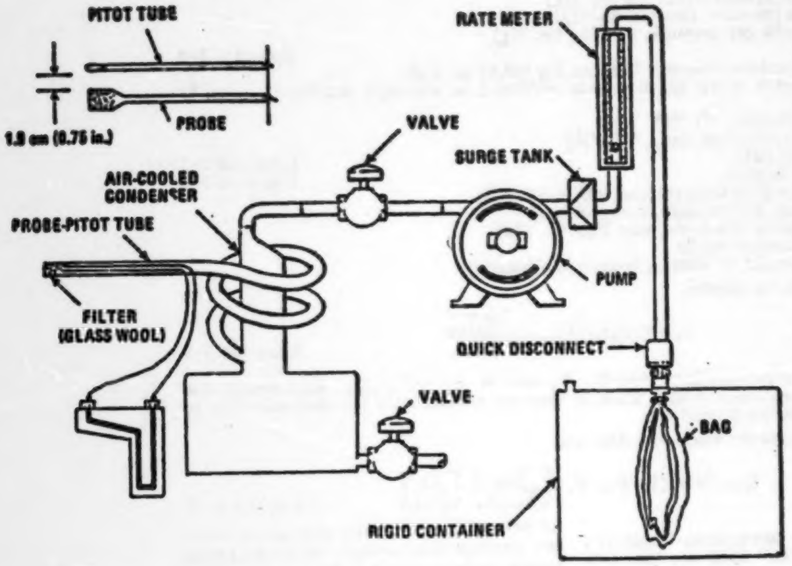

Figure 3-2. Integrated gas-sampling train.

2.2.2 Condenser—Air-cooled condenser, or equivalent, to remove excess moisture.

2.2.3 Valve—Needle valve, to adjust sample gas flow rate.

2.2.4 Pump—Leak-free, diaphragm type, or equivalent, to transport sample gas to the flexible bag. Install a small surge tank between the pump and rate meter to eliminate pulsation effect of diaphragm pump on the rotameter.

2.2.5 Rate meter—Potameter, capable of measuring a flow range from 0 to 1.0 litre per minute.

2.2.6 Flexible bag—Tedlar,[1] or equivalent, with a capacity in the range of 55 to 90 liters. Before each field test run make sure the bag is leak-free by checking it for leaks. To leak check, connect a water manometer and pressurize the bag to 5–10 cm H_2O (2–4 in. H_2O). Allow stand for 10 minutes. Any displacement in the water manometer indicates a leak.

NOTE.—An alternative leak check method is to pressurize the bag to 5–10 cm H_2O or 2–4 in. H_2O and allow to stand overnight. A deflated bag indicates a leak.

2.2.7 Pitot tube—Type S, or equivalent, attached to the probe to allow constant monitoring of the stack gas velocity so that the sampling flow rate can be regulated proportional to the stack gas velocity. The tips of the probe and pitot tube shall be adjacent to each other and the free space between them shall be about 1.9 cm (0.75 in.). When used with this method, the pitot tube need not be calibrated.

2.2.8 Differential pressure gauge—Inclined manometer capable of measuring velocity head to within 10% of the minimum measured value or ±0.013 mm (0.0005 in.), whichever is greater. Below a differential pressure of 1.3 mm (0.05 in.) water gauge, micromanometers with sensitivities of 0.013 mm (0.0005 in.) should be used. However, micromanometers may not easily be adaptable to the existing field conditions and are not easy to use with pulsating flow. Thus, alternative methods or other devices acceptable to the Administrator may be used when conditions warrant.

2.2.9 Manometer—About 28 cm (12 in.) water-filled U-tube manometer, or equivalent, to be used for the flexible bag leak check.

2.2.10 Vacuum gauge—At least 760 mm Hg (30 in. Hg) gauge, to be used for the sampling train leak check.

2.3 Analysis.

2.3.1 Orsat analyzer or Fyrite type combustion gas analyzer. The latter is used only for molecular weight determination. For low CO_2 (less than 4 percent) or high O_2 (greater than 15 percent) concentrations, the measuring burette of the Orsat must have at least 0.01% subdivisions.

3. *Sampling Procedure.*

3.1 Grab sampling. This procedure is primarily used for, but not limited to, determining molecular weight. Other uses must first be approved by the Administrator.

3.1.1 The sampling point in the duct shall be at the centroid of the cross section or at a point no closer to the walls than 1 m (3.28 ft), unless otherwise specified by the Administrator.

3.1.2 Set up the equipment as shown in Figure 3–1, making sure all connections are tight and leak-free by following the procedure in Section 4.

3.1.3 Place the probe in the stack at the sampling point and then purge the sampling line. Draw a sample into the analyzer and analyze according to Section 4.

3.2 Integrated sampling (required when the analytical results will be used to calculate a pollutant emission rate correction factor).

3.2.1 Select the sampling location according to Method 1. In addition to the criteria of Method 1, the sampling location shall be at least 2 diameters downstream from any point of air in-leakage. The downstream distance shall be calculated using the linear distance from the point of air in-leakage, and the diameter of the stack at the sampling location.

3.2.2 A minimum of 8 traverse points, selected according to Method 1, shall be used for circular stacks with diameters less than 0.6 m (2 ft.). A minimum of 12 traverse points, selected according to Method 1, shall be used for all other cases, unless otherwise specified in an applicable subpart, or unless specifically approved by the Administrator.

3.2.3 Leak check the flexible bag as in Section 2.2.6. Set up the equipment as shown in Figure 3–2. Just prior to sampling, leak check the train by placing a vacuum gauge at the condenser inlet pulling a vacuum of at least 250 mm Hg (10 in. Hg), plugging the outlet at the quick disconnect, and then turning off the pump. The vacuum shall remain stable for at least one minute. Evacuate the flexible bag. Connect the probe and place it in the stack and then purge the sampling line. Now, connect the bag and make sure that all connections are tight and leak free.

3.2.4 Sample at a rate proportional (within 20% of constant proportionality, or as specified by the Administrator) to the stack velocity, traversing all sampling points. Record proportional sampling data as shown in Figure 3–3. When analytical results will be used to calculate a pollutant emission rate correction factor, the sampling Must span the length of time the pollutant emission rate is being determined, sampling at each traverse point for an equal length of time. Collect at least 30 liters (1 ft³) of sample gas.

3.2.5 Obtain and analyze at least one integrated flue gas sample during each pollutant emission rate determination.

4. *Analytical Procedure.*

4.1 Leak check for Orsat analyzer. Moving an Orsat analyzer frequently causes it to leak. Therefore, an Orsat analyzer should be thoroughly leak-checked on-site before the flue gas sample is introduced into it. The suggested procedure for leak-checking an Orsat analyzer is:

4.1.1 Bring the liquid level in each pipette up to the reference mark on the capillary tubing and then close the pipette stopcock.

TIME	TRAVERSE PT.	Δp mm(in.) H_2O	Q 1pm	$R = \frac{Q}{\sqrt{\Delta p}}$	% DEV.[a]
			AVERAGE		

$$^{a}\%\,DEV = \left(\frac{R - R_{avg}}{R_{avg}}\right) 100 \quad (\text{MUST BE} \leq 20\%)$$

Figure 3-3. Proportional sampling data.

4.1.2 Raise the leveling bulb sufficiently to bring the confining liquid meniscus onto the graduated portion of the burette and then close the manifold stopcock.

4.1.3 Record the meniscus position.

4.1.4 Observe the meniscus in the burette and the liquid level in the pipette for movement over the next four minutes.

4.1.5 For the Orsat analyzer to pass the leak-check, two conditions must be met:

4.1.5.1 The liquid level in each pipette must not fall below the bottom of the capillary tubing during this four-minute interval.

4.1.5.2 The meniscus in the burette must not change by more than 0.2 ml during this four-minute interval. For the results to be valid the Orsat analyzer must pass this leak test before and after the analysis.

4.1.6 If the analyzer fails the leak-check procedure, all rubber connections and stopcocks should be checked until the cause of the leak is identified. Leaking stopcocks must be disassembled, cleaned and regreased. Leaking rubber connections must be replaced. After the analyzer is reassembled, the leak-check procedure must be repeated.

4.2 Determination of stack gas molecular weight. (Orsat leak check described above is optional). Within eight hours after the sample is taken, analyze it for percent carbon dioxide and percent oxygen using either an Orsat analyzer or a Fyrite type combustion gas analyzer. Determine the percent of the gas that is nitrogen and carbon monoxide by subtracting the sum of the percent carbon dioxide and percent oxygen from 100 percent.

4.2.1 Grab samples—Repeat the sampling and analysis until the molecular weight from each of three consecutive grab samples differs from their means by no more than 0.3 grams/gram mole (0.3 pounds/pound mole).

4.2.2 Integrated samples—Repeat the analysis until the molecular weight for three consecutive analyses differs from their mean by no more than 0.3 gram/gram mole (0.3 pound/pound mole).

4.3 Determination of O_2, CO_2, or excess air for calculating pollutant emission rate correction factors.

NOTE.—The Fyrite type combustion gas analyzers are not acceptable for this purpose, unless otherwise approved by the Administrator. The results may also be used for determining stack gas molecular weight.

4.3.1 Leak check the Orsat analyzer as described in section 4.1. This procedure is mandatory.

4.3.2 Within four hours after the integrated sample is taken, analyze it for percent carbon dioxide and percent oxygen using an Orsat analyzer. To ensure complete absorption of these gases make repeated passes through the absorbing solution until two consecutive readings are the same. Several passes (3–4) should be made between readings. (If constant readings cannot be obtained after three consecutive readings, replace the absorbing solution.) Determine the percent of the gas that is nitrogen and carbon monoxide by subtracting the sum of the percent carbon dioxide and percent oxygen from 100 percent.

This procedure assumes that carbon monoxide concentration is negligible. If appreciable quantities are expected, alternate procedures subject to approval of the Administrator, must be used.

4.3.3 Repeat the analysis on the integrated sample until each of three consecutive analyses for percent carbon dioxide and percent oxygen differ by no more than 0.3 percent by volume when carbon dioxide is greater than 3% and 0.2 percent by volume when carbon dioxide is less than or equal to 3%.

5. *Calculations.*

5.1 Nomenclature:

M_d = Dry molecular weight (gram/gram mole)
$\%EA$ = Percent excess air
$\%CO_2$ = Percent carbon dioxide by volume (dry basis)
$\%O_2$ = Percent oxygen by volume (dry basis)
$\%N_2$ = Percent nitrogen by volume (dry basis)
0.264 = Ratio of oxygen to nitrogen in air, v/v
0.28 = Molecular weight of both nitrogen and CO divided by 100
0.32 = Molecular weight of oxygen divided by 100
0.44 = Molecular weight of carbon dioxide divided by 100

5.2 Excess air. Use equation 3–1 to calculate the percent excess air using the three consecutive analyses that meet the requirements of section 4.3.3. Then calculate the average percent excess air.

$$\%EA = \frac{\%O_2(100)}{0.264\ \%N_2 - \%O_2} \qquad \text{Equation 3–1}$$

NOTE.—The equation above assumes that carbon monoxide concentration is negligible. If appreciable carbon monoxide concentrations are expected, consult with the Administrator.

5.3 Dry molecular weight. Use equation 3-2 to calculate the dry molecular weights using data obtained from sections 4.2.1, 4.2.2, or 4.3.2 and 4.3.3, average the results and report to the nearest 0.1 g/g-mole (0.1 lb/lb-mole).

$$M_d = 0.44(\%CO_2) + 0.32(\%O_2) + 0.28(\%N_2 + \%CO) \qquad \text{Equation 3-2}$$

5.4 Carbon dioxide concentration calculation. Using the three consecutive carbon dioxide analyses that meet the requirements of section 4.3.3, calculate the average carbon dioxide concentration.

6. *References.*

6.1 Altshuller, A. P. Storage of Gases and Vapors in Plastic Bags, International Journal of Air and Water Pollution, *6*, 75–81 (1963).

6.2 Connor, William D. and J. S. Nader, Air Sampling with Plastic Bags, Journal of the American Industrial Hygiene Association, *25*, 291–297 (1964).

6.3 "Burrell Manual for Gas Analysts," Seventh edition (1951), Available from Burrell Corporation, 2223 Fifth Avenue, Pittsburgh, Penna. 15219.

METHOD 4—DETERMINATION OF MOISTURE IN STACK GASES

1. *Principle and Applicability.*

1.1 Principle. A gas sample is extracted proportionally from the source and moisture is removed from the gas stream, condensed, and determined either volumetrically or gravimetrically.

1.2 Applicability. This method is applicable for the determination of moisture in stack gas.

Two methods are given. One is a reference method for the accurate determination of moisture content as needed to calculate emission data. The other is an approximation method for moisture content to be subsequently used for setting isokinetic sampling rates. For this latter purpose, the tester may use any alternate means for approximating the moisture content, e.g. drying tubes, wet bulb-dry bulb technique, condensation techniques, stoichiometric calculations, previous experience, etc. However, the actual isokinetic rate maintained during a pollutant sampling run and the moisture content used to calculate emission data will not be based on the results of the approximation method (see exception in note below), but will be determined from the data of the reference method, which is normally conducted simultaneously with a pollutant measurement run.

NOTE.—Any of the approximation methods which are shown to the satisfaction of the Administration of yielding results to within 1% H_2O of the reference method results may be used in lieu of the reference method.

These methods are not applicable to gas streams that contain liquid droplets. For these cases, assume that the gas stream is saturated. Determine the average stack gas temperature using gauges described in Method 2 and by traversing according to Method 1. Then obtain the moisture percentage by (1) using a psychometric chart and making appropriate corrections, if stack pressure is different from that of the chart, for absolute pressure or (2) by using saturation vapor pressure tables.

2. *Reference Method.*

The procedure for determining moisture content described in Method 5 is acceptable as a reference method.

2.1 Apparatus. A schematic of the sampling train used in this reference method is shown in *Figure* 4–1. All components shall be maintained and calibrated according to the procedure outlined in Method 5.

2.1.1 Probe—Stainless steel or glass tubing, sufficiently heated to prevent water condensation and equipped with a filter (either in-stack or heated out-stack) to remove particulate matter.

2.1.2 Condenser—Any system that cools the sample gas stream and allows measurement of the water condensed and moisture leaving the condenser, each to within 1 ml or 1 g. Acceptable means are to measure the condensed water either gravimetrically or volumetrically and to measure the moisture leaving the condenser by (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law or (2) by passing the sample gas stream through a tared silica gel trap with exit gases kept below 20° C (68° F) and determining the weight gain.

2.1.3 Cooling system—Ice bath container and crushed ice, or equivalent, to aid in condensing moisture.

2.1.4 Drying tube—Tube packed with 6–16 mesh indicating-type silica gel, or equivalent, to dry the sample gas and protect the pump and dry gas meter. This may be an integral part of the condenser system, in which case the tube shall be immersed in the ice bath and a thermometer placed at the outlet for monitoring purposes. If approach (1) of section 2.1.2 is used to measure the moisture leaving the condenser, the temperature and pressure must be monitored before the silica gel tube.

2.1.5 Metering system—Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3° C (5.4° F), dry gas meter with ±2 percent accuracy, and related equipment, or other metering systems approved by the Administrator, as required to maintain a proportional sampling rate and to determine sample gas volume.

2.1.6 Barometer—Mercury, aneroid, or other barometers capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby weather bureau station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and the sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

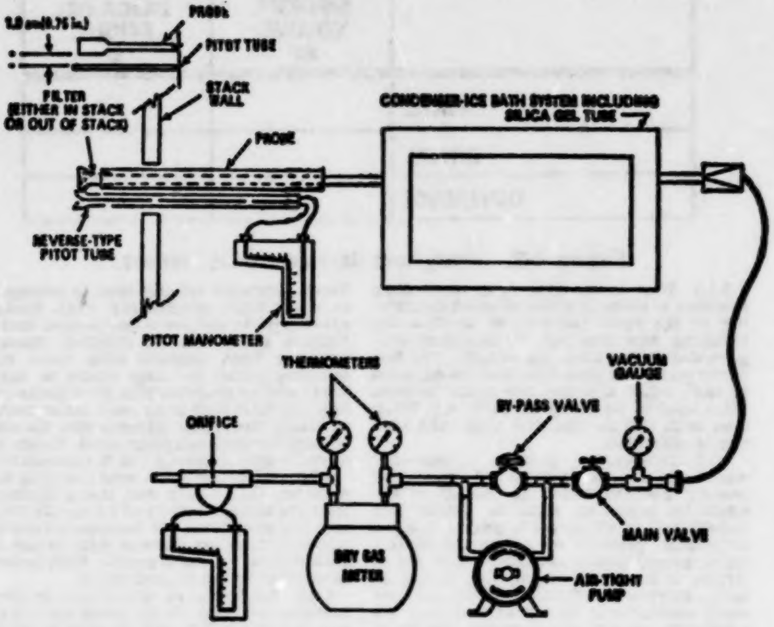
1.9 cm (0.75 in.)
PROBE
PITOT TUBE
FILTER (EITHER IN STACK OR OUT OF STACK)
STACK WALL
PROBE
REVERSE-TYPE PITOT TUBE
PITOT MANOMETER
CONDENSER-ICE BATH SYSTEM INCLUDING SILICA GEL TUBE
THERMOMETERS
VACUUM GAUGE
BY-PASS VALVE
ORIFICE
MAIN VALVE
DRY GAS METER
AIR-TIGHT PUMP

Figure 4-1. Moisture sampling train-reference method.

PLANT ______________________
LOCATION ______________________
OPERATOR ______________________
DATE ______________________
RUN NO. ______________________
AMBIENT TEMPERATURE ______________________
BAROMETRIC PRESSURE ______________________
PROBE LENGTH m(ft) ______________________

SCHEMATIC OF STACK CROSS SECTION

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	STACK TEMPERATURE °C (°F)	VELOCITY HEAD (ΔPs), mm(in.) H2O	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER (ΔH), mm(in.) H2O	GAS SAMPLE VOLUME m³ (ft³)	GAS SAMPLE TEMPERATURE AT DRY GAS METER		TEMPERATURE OF GAS LEAVING CONDENSER OR LAST IMPINGER, °C (°F)
						INLET (Tm in), °C (°F)	OUTLET (Tm out), °C (°F)	
TOTAL						Avg.	Avg.	
AVERAGE						Avg.		

Figure 4-2. Field moisture determination-reference method.

	IMPINGER VOLUME, ml	SILICA GEL WEIGHT, g
FINAL		
INITIAL		
DIFFERENCE		

Figure 4-3. Analytical data-reference method.

2.1.7 Pitot tube—Type S, or equivalent, attached to probe to allow constant monitoring of the stack gas velocity so that the sampling flow rate can be regulated proportional to the stack gas velocity. The tips of the probe and pitot tube shall be adjacent to each other and the free space between them shall be about 1.9 cm (0.75 in.). When used with this method, the pitot tube need not be calibrated.

2.1.8 Differential pressure guage—Inclined manometer capable of measuring velocity head to within 10 percent of the minimum measured value or ±0.013 mm (0.0005 in.), in whichever is greater. Below a differential pressure of 1.3 mm (0.05 in.) water gauge, micromanometers with sensitivities of 0.013 mm (0.0005 in.) should be used. However, micromanometers are not easily adaptable to field conditions and are not easy to use with the pulsating flow. Thus, methods or other devices acceptable to the Administrator may be used when conditions warrant.

2.1.9 Temperature gauge—Thermocouple, liquid filled bulb thermometer, bimetallic thermometer, mercury-in-glass thermometer, or other gauges that are capable of measuring temperature to within 1.5 percent of the minimum absolute stack temperature.

2.1.10 Graduated cylinder and/or balance—To measure condensed water and moisture caught in the silica gel to within 1 ml or 1 g. Graduated cylinders shall have subdivisions no greater than 2 ml. Most laboratory balances are capable of weighing to the nearest 0.5 g or less. These balances are suitable for use here.

2.1.11 Temperature and pressure gauges—If Dalton's law is used to monitor temperature and pressure at condenser outlet. The temperature gauge shall have an accuracy of 1° C (2° F). The pressure gauge shall be capable of measuring pressure to within 2.5 mm Hg (0.1 in. Hg).

2.1.12 Silica gel—If used to measure moisture leaving condenser, indicating type, 6–16 mesh. If previously used, dry at 175° C (350° F) for 2 hours. New silica gel may be used as received.

2.2 Procedure. The procedure below is written for a condenser system incorporating silica gel and gravimetric analysis to measure the moisture leaving the condenser and volumetric analysis to measure the condensed moisture.

2.2.1 Select the sampling site and minimum number of sampling points according to Method 1 or as specified by the Administrator. Determine the range of velocity head using Method 2 for the purpose of making proportional sampling rate calculations. Select a suitable velocity head to correspond to about 0.014 m³/min (0.5 cfm). Select a suitable probe and probe length such that all traverse points can be sampled. Consider sampling from opposite sides (four total sampling ports) for large stacks to enable use of shorter probe lengths. Mark probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point. Weigh and record weight of silica gel to the nearest 0.5 g.

2.2.2 Select a suitable total sampling time of no less than 1 hour such that a minimum total gas sample volume of 0.6 m³ (20 ft³) at standard conditions will be collected and the sampling time per traverse point is not less than 2 min., or some greater time interval as specified by the Administrator.

2.2.3 Set up the sampling train as shown in Figure 4–1. Turn on the probe heating system to about 120° C (248° F) so as to prevent water condensation and allow time for temperature to stabilize. Place crushed ice in the ice bath container. Leak check the train by plugging the probe inlet and pulling a 380 mm Hg (15 in. Hg) vacuum. A leakage rate in excess of 4 percent of the average sampling rate or 0.00057 m³/min. (0.02 cfm), whichever is less, is unacceptable.

2.2.4 During the sampling run, maintain a sampling rate within 20 percent, or as specified by the Administrator, of constant proportionality. For each run, record the data required on the example data sheet shown in Figure 4–2. Be sure to record the initial dry gas meter reading. Record the dry gas meter reading at the beginning and end of each sampling time increment, when changes in flow rates are made, and when sampling is halted. Take other data point readings at each sample point at least once during each time increment.

2.2.5 To begin sampling position the probe tip at the first traverse point. Immediately start the pump and adjust the flow to proportional conditions. Traverse the cross section. Add more ice and, if necessary, salt to maintain a temperature of less than 20° C (68° F) at the silica gel outlet to avoid excessive moisture losses.

2.2.6 After collecting the sample, measure the volume increase of the liquid to the nearest 1 ml. Determine the increase in weight of the silica gel tube to the nearest 0.5 g. Record the information (see example data sheet, Figure 4–3) and calculate the moisture percentage.

2.3 Calculations. Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

2.3.1 Nomenclature.

B_{ws} = Proportion by volume
M_w = Molecular weight of water, 18 g/g-mile (18 lb/lb-mole)
P_m = Absolute pressure (for this method, same as barometric pressure) at the dry gas meter, mm Hg (in. Hg)
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg)
R = Ideal gas constant, 0.06236 (mm hg)(m³)/(g-mole)(°K) for metric units and 21.83 (in. Hg)(ft³)/(lb-mole)/(lb-mole)(°R) for English units
T_m = Absolute temperature at meter, °K (°R)
T_{std} = Absolute temperature, 293° K (528° R)
V_m = Dry gas volume measured by meter, dcm (dcf)
$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf)
$V_{wc(std)}$ = Volume of water vapor condensed corrected to standard conditions, m³ (ft³)
$V_{wsg(std)}$ = Volume of water vapor collected in silica gel corrected to standard conditions, m³ (ft³)
V_f = Final volume of condenser contents, ml
V_i = Initial volume, if any, of condenser contents, ml
W_f = Final weight of condenser contents, g
W_i = Initial weight of condenser contents, g
ρ_w = Density of water, 1 g/ml (0.00220 lb/ml)

2.3.2 Volume of water vapor condensed.

$$V_{wc(std)}=\frac{(V_f-V_i)\rho_w RT_{std}}{P_{std}M_w}$$

$$=K(V_f-V_i) \quad \text{Equation 4-1}$$

where:

K=0.00134 m³/ml for metric units

=0.0472 ft³/ml for English units

2.3.3 Volume of water vapor collected in silica gel.

$$V_{wsg(std)}=\frac{(W_f-W_i)RT_{std}}{P_{std}M_w}$$

$$=K(W_f-W_i)$$

Equation 4-2

where:

K=0.00134 m³/g for metric units

=0.0472 ft³/g for English units

2.3.4 Gas volume.

$$V_{m(std)}=V_m\frac{(P_m)(T_{std})}{(P_{std})(T_m)}$$

$$=K\frac{V_mP_m}{T_m} \quad \text{Equation 4-3}$$

where:
K=0.3855 °K/mm Hg for metric units
=17.65 °R/in. Hg for English units

2.3.5 Moisture Content:

$$B_{ws}=\frac{V_{wc}+V_{wsg}}{V_{wc}+V_{wsg}+V_{mc}}$$

Equation 4-4

2.3.6 Proportional sampling constant—For each time increment, calculate

$$V_m/\sqrt{\Delta_p}.$$

Calculate the average. If the value for any time increment falls beyond 20 percent of the average, reject the results and do run over.

3. *Approximation Method.*

The approximation method described below is presented only as a suggested method.

3.1 Apparatus.

3.1.1 Probe—Stainless steel or glass tubing sufficiently heated to prevent water condensation and equipped with a filter (either in-stack or heated out-stack) to remove particulate matter.

3.1.2 Impingers—Two midget impingers, each with 30 ml capacity, or equivalent.

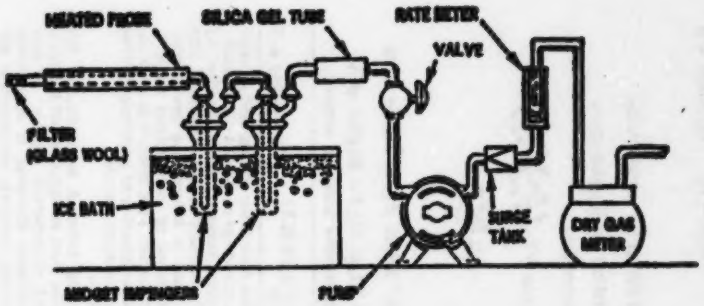

Figure 4-4. Moisture-sampling train.

LOCATION______________ COMMENTS
TEST______________
DATE______________
OPERATOR______________
BAROMETRIC PRESSURE______________

CLOCK TIME	GAS VOLUME THROUGH METER, (Vm), m³ (ft³)	RATE METER SETTING m³/min. (ft³/min.)	METER TEMPERATURE, °C (°F)

Figure 4-5. Field moisture determination.

3.1.3 Ice bath—Container and ice, to aid in condensing moisture in impingers.

3.1.4 Drying tube—Tube packed with 6–16 mesh indicating-type silica gel, or equivalent, to dry the sample gas and to protect the meter and pump.

3.1.5 Valve—Needle valve, to regulate sample gas flow rate.

3.1.6 Pump—Leak-free, diaphragm type, or equivalent, to pull gas through the train.

3.1.7 Volume meter—Dry gas meter, sufficiently accurate to measure the sample volume within 2 percent, and calibrated over the range of flow rates and conditions actually used during sampling.

3.1.8 Rate meter—Rotameter, to measure the flow range from 0 to 3 lpm (0 to 0.11 cfm).

3.1.9 Graduated cylinder—25 ml.

3.1.10 Barometer—Mercury, aneroid, or other barometers capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby weather bureau station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

3.1.11 Vacuum gauge—At least 760 mm Hg (30 in. Hg) gauge, to be used for the sampling leak check.

3.2 Procedure.

3.2.1 Place exactly 5 ml distilled water in each impinger. Assemble the apparatus without the probe as shown in Figure 4–4. Leak check by placing a vacuum gauge at the inlet to the first impinger and drawing a vacuum of at least 250 mm Hg (10 in. Hg), plugging the outlet of the rotameter, and then turning off the pump. The vacuum shall remain constant for a least one minute. Carefully release the vacuum gauge before releasing the rotameter end.

3.2.2 Connect the probe and sample at a constant rate of 2 lpm (0.071 cfm). Continue sampling until the dry gas meter registers about 30 liters (1.1 ft³) or until visible liquid droplets are carried over from the first impinger to the second. Record temperature, pressure, and dry gas meter readings as required by Figure 4–5.

3.2.3 After collecting the sample, combine the contents of the two impingers and measure volume to the nearest 0.5 ml.

3.3 Calculations. The calculation method presented is designed to estimate the moisture in the stack gas and therefore other data, which are only necessary for accurate moisture determinations, are not collected. The following equations adequately estimate the moisture content for the purpose of determining isokinetic sampling rate settings.

3.3.1 Nomenclature.

B_{wm} = Approximate water vapor in the gas stream leaving the impinger, 0.025 proportion by volume

B_{wo} = Water vapor in the gas stream, proportion by volume

M_w = Molecular weight of water, 18 g/g-mole (18 lb/lb-mole)

P_m = Absolute pressure (for this method, same as barometric pressure) at the dry gas meter

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg)

P = Ideal gas constant, 0.06236 (mm Hg)(m³)/(g-mole)(°K) for metric units and 21.83 (in. Hg) (ft³)/(lb-mole)(°R) for English units

T_m = Absolute temperature at meter, °K (°R)

T_{std} = Standard absolute temperature, 293° K (528° R)

V_f = Final volume of impinger contents, ml

V_i = Initial volume of impinger contents, ml

V_m = Dry gas volume measured by dry gas meter, dcm (dcf)

$V_{m(std)}$ = Dry gas volume measured by dry gas meter, corrected to standard conditions, dscm (dscf)

$V_{wc(std)}$ = Volume of water vapor condensed, corrected to standard conditions, m³ (ft³)

ρ_w = Density of water, 1 g/ml (0.00220 lb/ml)

3.3.2 Volume of water vapor collected.

$$V_{wc} = \frac{(V_f - V_i)\rho_w R T_{std}}{P_{std} M_w}$$

$$= K(V_f - V_i) \qquad \text{Equation 4-5}$$

Where:

K = 0.00134 m³/ml for metric units

= 0.0472 ft³/ml for English units

3.3.3 Gas volume.

$$V_{m(std)} = V_m \left(\frac{P_m}{P_{std}}\right)\left(\frac{T_{std}}{T_m}\right)$$

$$= K \frac{V_m P_m}{T_m}$$

where:

K = 0.3855 °K/mm Hg for metric units

= 17.65 °R/in. Hg for English units

3.3.4 Approximate moisture content.

$$B_{wo} = \frac{V_{wc}}{V_{wc} + V_{m(std)}} + B_{wm} = \frac{V_{wc}}{V_{wc} + V_{m(std)}} + (0.025) \qquad \text{Equation 4-7}$$

4. *Calibration.*

4.1 Use methods and equipment as specified in Methods 2 and 5 and APTD–0576 to calibrate dry gas meter, barometer, and thermometers.

5. *References.*

5.1 Air Pollution Engineering Manual, Danielson, J. A. (ed.), U.S. DHEW, PHS, National Center for Air Pollution Control, Cincinnati, Ohio, PHS Publication No. 999–AP–40, 1967.

5.2 Devorkin, Howard, et al., Air Pollution Source Testing Manual, Air Pollution Control District, Los Angeles, Calif., November 1963.

5.3 Methods for Determination of Velocity, Volume, Dust and Mist Content of Gases, Western Precipitation Division of Joy Manufacturing Co., Los Angeles, Calif., Bulletin WP–50, 1968.

METHOD 5—DETERMINATION OF PARTICULATE EMISSION FROM STATIONARY SOURCES

1. *Principle and Applicability.*

1.1 Principle. Particulate matter is withdrawn isokinetically from the source and collected on glass fiber filter maintained at temperatures in the range of 120±14° C (248±25° F) or such other temperature as specified by an applicable subpart of the standards. The particulate mass is determined gravimetrically after removal of uncombined water.

1.2 Applicability. This method is applicable for the determination of particulate emissions from stationary sources.

2. *Apparatus.*

2.1 Sampling train. A schematic of the sampling train used in this method is shown in Figure 5–1. Commercial models of this train are available. However, if one desires to build his own, complete construction details are described in APTD–0581; for changes from the APTD–0581 document and for allowable modifications to Figure 5–1, see the following subsections.

The operating and maintenance procedures for the sampling train are described in APTD–0576. Since correct usage is important in obtaining valid results, all users should read the APTD–0576 document and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein.

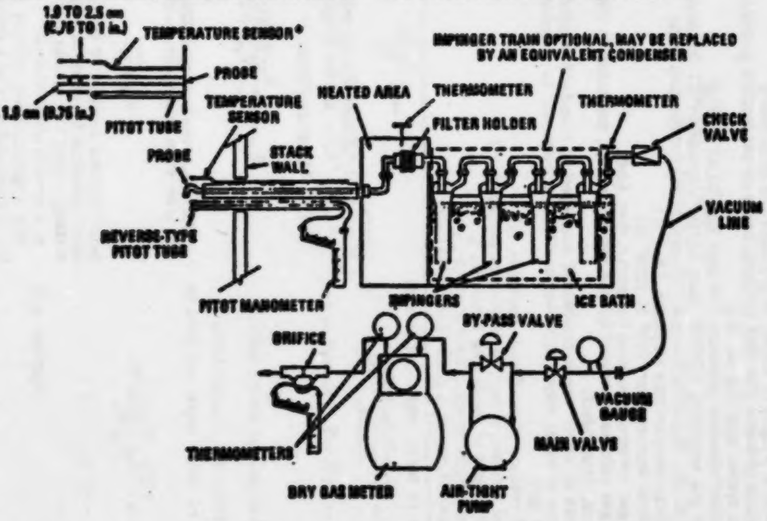

Figure 5-1. Particulate-sampling train.

*If difficulty is expected in inserting the temperature sensor-pitot tube-probe assembly into the stack due to spacing requirements, the temperature sensor may be located between the probe and pitot tube so that the tip of the temperature sensor is no closer than 5cm (2 in.) from the tip of the pitot tube.

2.1.1 Probe nozzle—Stainless steel (316) with sharp, tapered leading edge. The angle of taper shall be ≤30° and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise approved by the Administrator. The nozzle shall be constructed from seamless stainless steel tubing. Other configurations and construction material may be used subject to approval from the Administrator.

A range of sizes suitable for isokinetic sampling should be available, e.g., 0.32 cm (⅛ in.) up to 1.27 cm (½ in.) (or larger if higher volume sampling trains are used) inside diameter (ID) nozzles in increments of 0.16 cm (1/16 in.). Each nozzle shall be calibrated according to the procedures outlined in the calibration section.

2.1.2 Probe liner—Borosilicate or quartz glass tubing with a heating system capable of maintaining a gas temperature at the exit end during sampling of no greater than 120±14° C (248±25° F) or no greater than such other temperature as specified by an applicable subpart of the standards. Since the actual temperature at the outlet of the probe is not monitored during sampling, probes constructed according to APTD–0581 and utilizing the calibration curves of APTD–0576 or calibrated according to the procedure outlined in APTD–0576 will be considered as acceptable.

Borosilicate or quartz glass probe liners shall be used for temperatures up to about 480° C (900° F) and quartz liners for temperatures up to about 900° C (1650° F). Both may be used at higher temperatures for short periods of time, but must be approved by the Administrator. The softening temperature for borosilicate is 820° C (1508° F) and for quartz it is 1500° C (2732° F).

When length limitations, i.e. greater than about 2.5 m (8.2 ft), are encountered at temperatures less than 320° C (608° F), stainless steel (316) or Incoloy 825[1] (both of seamless tubing), or other materials as approved by the Administrator, may be used. Metal probes for sampling gas streams at temperatures in excess of 320° C (608° F) must be approved by the Administrator.

2.1.3 Pitot tube—Type S, or other device approved by the Administrator, attached to probe to allow constant monitoring of the stack gas velocity. The face openings of the pitot tube and the probe nozzle shall be adjacent and parallel to each other, not necessarily on the same plane, during sampling. The free space between the nozzle and pitot tube shall be at least 1.9 cm (0.75 in.). The free space shall be set based on a 1.3 cm (0.5 in.) ID nozzle. If the sampling train is designed for sampling at higher flow rates than that described in APTD–0581, thus necessitating the use of larger sized nozzles, the largest sized nozzle shall be used to set the free space.

The pitot tube must also meet the criteria specified in Method 2 and calibrated according to the procedure in the calibration section of that method.

2.1.4 Differential pressure gauge—Inclined manometer capable of measuring velocity head to within 10 percent of the minimum measured value or ±0.013 mm (0.005 in.), whichever is greater. Below a differential pressure of 1.3 mm (0.05 in.) water gauge, micromanometers with sensitivities of 0.013 mm (0.0005 in.) should be used. However, micromanometers are not easily adpatable to field conditions and are not easy to use with pulsating flow. Thus, methods or other devices acceptable to the Administrator may be used when conditions warrant.

2.1.5 Filter holder—Borosilicate glass frit filter support and a silicone rubber gasket. Other materials of construction may be used with approval from the Administrator, e.g., if probe liner is stainless steel, then the filter holder may be stainless steel. The holder design shall provide a positive seal against leakage from the outside or around the filter.

2.1.6 Filter heating system—Any heating system capable of maintaining a temperature around the filter holder during sampling of no greater than 120±14° C (248 ±25° F), or such other temperature as specified by an appplicable subpart of the standards. A temperature gauge capable of measuring temperature to within 30° C (5.4° F) shall be installed such that temperature around the filter holder can be regulated and monitored during sampling. Heating systems other than shown in APTD–0581 may be used.

2.1.7 Condenser—Any system that cools the sample gas stream and allows measurement of the water condenser and moisture leaving the condenser, each to within 1 ml or 1 g. Acceptable means are to measure the condensed water either gravimetrically or volumetrically and to measure the moisture leaving the condenser by (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law or (2) by passing the sample gas stream through a tared silica gel trap with exit gases kept below 20° C (68° F) and determining the weight gain.

Note.—If "condensible particulate matter" is desired, in addition to moisture content, the following system shall be used—four impingers connected in series with ground glass, leak free fittings or any similarly leak free noncontaminating fittings. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with a 1.3 cm (½ in.) ID glass tube extending to about 1.3 cm (½ in.) from the bottom of the flask. The second impinger shall be of the Greenburg-Smith design with the standard tip. Individual States or control agencies requiring this information shall be contacted as to the sample recovery and analysis of the impinger contents.

For purposes of writing the procedure of this method, the system described in the note above will be used for determining the moisture content of the stack gas. Modifications (e.g. using flexible connections between the impingers or using materials other than glass) may be used with approval from the Administrator.

If means other than silica gel are used to determine the amount of moisture leaving the condenser, it is recommended that silica gel still be used between the condenser system and pump to prevent moisture condensation in the pump and metering devices.

Unless otherwise specified by the Administrator, flexible vacuum lines may be used to connect the filter holder to the condenser.

2.1.8 Metering system—Vacuum gauge, leak-free pump, thermometers capable of measuring temperature within 3° C (5.4° F), dry gas meter with 2 percent accuracy, and related equipment, or equivalent, as required to maintain an isokinetic sampling rate and to determine sample volume. Sampling trains utilizing metering systems designed for higher flow rates than that described in APTD–0581 or APTD–0576 may be used provided that the specifications in section 2 of this method are met. When the metering system is used in conjunction with a pitot tube, the system shall enable checks of isokinetic rates.

2.1.9 Barometer—Mercury, aneroid, or other barometers capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby weather bureau station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.1.10 Gas density determination equipment—Temperature and pressure gauges and gas analyzer as described in Methods 2 and 3.

2.1.11 Temperature and pressure gauges—If Dalton's law is used to monitor temperature and pressure at condenser outlet. The temperature gauge shall have an accuracy of 1° C (2° F). The pressure gauge shall be capable of measuring pressure to within 2.5 mm Hg (0.1 in. Hg). If silica gel is used in the condenser system the temperature and pressure must be measured before the silica gel component.

2.2 Sample recovery.

2.2.1 Probe liner and probe nozzle brushes—Nylon bristles with stainless steel wire handles. The probe brush shall have extensions, at least as long as the probe, of stainless steel, nylon, teflon, or similarly inert material. Both brushes shall be properly sized and shaped to brush out the probe liner and nozzle.

2.2.2 Glass wash bottles—Two.

2.2.3 Glass sample storage containers—Chemically resistant, borosilicate glass bottles, for acetone washes, 500 ml or 1,000 ml. Screw cap closures shall be teflon rubber-backed liners or of such construction so as to be leak free and prevent chemical attack from the acetone. (Narrow mouth glass bottles have been found to be less prone to leakage.) Other types of containers must be approved by the Administrator.

2.2.4 Petri dishes—For filter samples, glass or polyethylene, unless otherwise specified by the Administrator.

2.2.5 Graduated cylinder and/or balance—To measure condensed water to within 1 ml or 1 g. Graduated cylinders shall have subdivisions no greater than 2 ml. Most laboratory balances are capable of weighing to the nearest 0.5 g or less. Any of these balances are suitable for use here and in section 2.3.4.

2.2.6 Plastic storage containers—Air tight containers to store silica gel.

2.2.7 Funnel and rubber policeman—To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

2.3 Analysis.

2.3.1 Glass weighing dishes.

2.3.2 Desiccator.

2.3.3 Analytical balance—To measure to within 0.1 mg.

2.3.4 Balance—To measure to within 0.5 g.

2.3.5 Beakers—250 ml.

2.3.6 Hygrometer—To measure the relative humidity of the laboratory environment.

2.3.7 Temperature gauge—To measure the temperature of the laboratory environment.

3. *Reagents.*

3.1 Sampling.

3.1.1 Filters—Glass fiber filters, without organic binder exhibiting at least 99.95 percent efficiency (≤0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D 2986–71. Test data from the supplier's quality control program is sufficient for this purpose.

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[1] Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

3.1.2 Silica gel—Indicating type, 6–16 mesh. If previously used, dry at 175° C (350° F) for 2 hours. New silica gel may be used as received.

3.1.3 Water—When analysis of the material caught in the impingers is required, distilled water shall be used. Run blanks prior to field use to eliminate a high blank on test samples.

3.1.4 Crushed ice.

3.1.5 Stopcock grease—Acetone insoluble, heat stable silicone grease. This is not necessary if screw-on connectors with teflon sleeves, or similar, are used.

3.2 Sample recovery.

3.2.1 Acetone—Reagent grade, ≤0.001 percent residue, in glass bottles. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers. Thus, acetone blanks shall be run prior to field use and only acetone with low blank values (≤0.001 percent) shall be used.

3.3 Analysis.

3.3.1 Acetone—Same as 3.2.1.

3.3.2 Desiccant—Anhyrdous calcium sulfate, indicating type.

4. *Procedure.*

4.1 Sampling. The sampling shall be conducted by competent personnel experienced with this test procedure.

4.1.1 Pretest preparation. All the components shall be maintained and calibrated according to the procedure described in APTD–0576, unless otherwise specified herein.

Weigh approximately 200–300 g of silica gel in air tight containers to the nearest 0.5 g. Record the total weight, both silica gel and container, on the container. More silica gel may be used but care should be taken during sampling that it is not entrained and carried out from the impinger. As an alternative, the silica gel may be weighed directly in the impinger or its sampling holder just prior to the train assembly.

Check filters visually against light for irregularities and flaws or pinhole leaks. Label a filter of proper diameter on the back side near the edge using numbering machine ink. As an alternative, label the shipping container (glass or plastic petri dishes) and keep the filter in this container at all times except during sampling and weighing.

Desiccate the filters at 20±5.6° C (68±10° F) and ambient pressure for at least 24 hours and weigh at 6 or more hour intervals to a constant weight, i.e., ≤0.5 mg change from previous weighing, and record results to the nearest 0.1 mg. During each weighing the filter must not be exposed to the laboratory atmosphere for a period greater than 2 minutes and a relative humidity above 50 percent.

4.1.2 Preliminary determinations. Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2 and moisture content using Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate calculations. Estimates may be used. However, final results will be based on actual measurements made during the test.

Select a nozzle size based on the range of velocity heads such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the differential pressure gauge is capable of measuring the minimum velocity head value to within 10 percent, or as specified by the Administrator.

Select a suitable probe liner and probe length such that all traverse points can be sampled. Consider sampling from opposite sides for large stacks to reduce the length of probes.

Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that the sampling time per point is not less than 2 min. or some greater time interval as specified by the Administrator and the sample volume that will be taken will exceed the required minimum total gas sample volume specified in the test procedures for the specific industry. The latter is based on an approximate average sampling rate. Note also that the minimum total sample volume is corrected to standard conditions.

It is recommended that ½ or an integral number of minutes be sampled at each point in order to avoid timekeeping errors.

In some circumstances, e.g. batch cycles, it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the Administrator's approval must first be obtained.

4.1.3 Preparation of collection train. During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.

Place 100 ml of water in each of the first two impingers, leave the third impinger empty, and place approximately 200–300 g or more, if necessary, of preweighed silica gel in the fourth impinger. Record the weight of the silica gel and container to the nearest 0.5 g. Place the container in a clean place for later use in the sample recovery.

Using a tweezer or clean disposable surgical gloves, place the labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as not to allow the sample gas stream to circumvent the filter. Check filter for tears after assembly is completed.

When glass liners are used, install selected nozzle using a Viton A[1] O-ring when stack temperatures are less than 260° C (500° F) or an asbestos string gasket when temperatures are higher. The Viton A O-ring and asbestos string gasket are installed as a seal where the nozzle is connected to a glass liner. See APTD–0576 for details. When metal liners are used, install the nozzle as above or by a leak free direct mechanical connection. Mark probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

Unless otherwise specified by the Administrator, attach a temperature probe to the metal sheath of the sampling probe so that the sensor extends beyond the probe tip and does not touch any metal. Its position should be about 1.9 to 2.54 cm (0.75 to 1 in.) from both the pitot tube and probe nozzle to avoid interference with the gas flow.

Set up the train as in Figure 5–1, using, if necessary, a very light coat of silicone grease on all ground glass joints, greasing only the outer portion (see APTD–0576) to avoid possibility of contamination by the silicone grease. With approval from the Administrator, a glass cyclone may be used between the probe and filter holder.

Place crushed ice around the impingers.

4.1.4 Leak check procedure—After the sampling train has been assembled, turn on and set the filter and probe heating system to the power required to reach a temperature of 120±14° C (248±25° F) or such other temperature as specified by an applicable subpart of the standards for the leak check. (If water condensation is not a problem the probe and/or filter heating system need not be used.) Allow time for the temperature to stabilize. If a Viton A O-ring or other leak free connection is used in assembling the probe nozzle to the probe liner, leak check the train at the sampling site by plugging the nozzle and pulling a 380 mm Hg (15 in. Hg) vacuum.

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[1] Mention of trade names is not intended to constitute endorsement by EPA.

NOTE.—A lower vacuum may be used provided that it is not exceeded during the test.

If an asbestos string is used, do not connect the probe to the train during the leak check. Instead, leak check the train as above by first plugging the inlet to the filter holder. Then connect the probe to the train and leak check at about 25 mm Hg (1 in. Hg) vacuum. A leakage rate in excess of 4 percent of the average sampling rate or 0.00057 m^3/min. (0.02 cfm), whichever is less, is unacceptable in either case.

PLANT ______________
LOCATION ______________
OPERATOR ______________
DATE ______________
RUN NO. ______________
SAMPLE BOX NO. ______________
METER BOX NO. ______________
METER $\Delta H_@$ ______________
C FACTOR ______________
PITOT TUBE COEFFICIENT, C_p ______________

SCHEMATIC OF STACK CROSS SECTION

AMBIENT TEMPERATURE ______________
BAROMETRIC PRESSURE ______________
ASSUMED MOISTURE, % ______________
PROBE LENGTH, m (ft) ______________
NOZZLE IDENTIFICATION NO. ______________
AVERAGE CALIBRATED NOZZLE DIAMETER, cm (in.) ______________
PROBE HEATER SETTING ______________
LEAK RATE, m^3/min (cfm) ______________
PROBE LINER MATERIAL ______________

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	STATIC PRESSURE mm Hg (in Hg)	STACK TEMPERATURE (T_S) °C (°F)	VELOCITY HEAD (ΔP_S), mm (in.) H_2O	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER mm H_2O (in. H_2O)	GAS SAMPLE VOLUME m^3 (ft^3)	GAS SAMPLE TEMPERATURE AT DRY GAS METER		FILTER HOLDER TEMPERATURE, °C (°F)	TEMPERATURE OF GAS LEAVING CONDENSER OR LAST IMPINGER, °C (°F)
							INLET °C (°F)	OUTLET °C (°F)		
TOTAL							Avg.	Avg.		
AVERAGE	–						Avg.			

Figure 5-2. Particulate field data.

The following leak check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with by-pass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the by-pass valve until 380 mm Hg (15 in. Hg) vacuum is reached. Do not reverse direction of by-pass valve. This will cause water to back up into the filter holder. If 380 mm Hg (15 in. Hg) is exceeded, either leak check at this higher vacuum or end the leak check as shown below and start over.

When the leak check is completed, first slowly remove the plug from the inlet to the probe or filter holder and immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the filter holder and silica gel from being entrained backward into the third impinger.

Leak checks shall be conducted as described whenever the train is disengaged, e.g. for silica gel or filter changes during the test, prior to each test run, and at the completion of each test run. If leaks are found to be in excess of the acceptable rate, the test will be considered invalid. To reduce lost time due to leakage occurrences, it is recommended that leak checks be conducted between port changes at the highest vacuum reading drawn during that sampling traverse.

4.1.5 Particulate train operation—During the sampling run, isokinetic sampling rate to within 10 percent, or as specified by the Administrator, of true isokinetic and the temperature around the filter of no greater than 120±14° C (248±25° F), or as specified by an applicable subpart of the standards, shall be maintained.

For each run, record the data required on the example data sheet shown in Figure 5-2. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, and when sampling is halted. Take other data point readings at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer.

Clean the portholes prior to the test run to minimize the chance of sampling the deposited material. To begin sampling, remove the nozzle cap, verify that the filter and probe are up to temperature, and that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediate start the pump and adjust the flow to isokinetic conditions. Nomographs are available for sampling trains using type S pitot tubes with 0.85±0.02 coefficient and when sampling in air or a stack gas with equivalent density (molecular weight equal to 29±4), which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. APTD-0576 details the procedure for using these nomographs. If C_p and M_d are outside the above stated ranges, do not use the nomograph unless appropriate steps (see Peference 7.7) are taken to compensate for the deviations.

When the stack is under significant negative stack pressure (height of impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack to avoid water backing into the filter holder. If necessary, the pump may be turned on with the coarse adjust valve closed.

When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

Traverse the stack cross section, as required by Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the portholes, to minimize chance of extracting deposited material.

During the test run, make periodic adjustments to keep the temperature around the filter holder at the proper temperature and add more ice and, if necessary, salt to maintain a temperature of less than 20°C (68°F) at the condenser/silica gel outlet to avoid excessive moisture losses. Also, periodically check the level and zero of the manometer.

If the pressure drop across the filter becomes too high making isokinetic sampling difficult to maintain, the filter may be replaced in the midst of a sample run. It is recommended that another complete filter assembly be used rather than attempting to change the filter itself. After the new filter or filter assembly is installed conduct a leak check. The particulate weight shall include the summation of all filter assembly catches.

A single train shall be used for the entire sample run, except for filter and silica gel changes. However, if approved by the Administrator, two or more trains may be used for a single test run when there are two or more ducts or sampling ports. The results shall be the total of all sampling train catches.

At the end of the sample run, turn off the pump, remove the probe and nozzle from the stack, and record the final dry gas meter reading. Perform a leak check at a vacuum equal to or greater than the maximum reached during sampling. Calculate percent isokinetic (see calculation section) to determine whether another test run should be made. If there is difficulty in maintaining isokinetic rates due to source conditions, consult with the Administrator for possible variance on the isokinetic rates.

4.2 Sample recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to prevent losing or gaining particulate matter. Do not cap off the probe tip tightly while the sampling train is cooling down as this would create a vacuum in the filter holder, thus drawing water from the impingers into the filter.

Before moving the sample train to the cleanup site, remove the probe from the sample train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate, if present. Wipe off the silicone grease from the filter inlet where the probe was fastened and cap it. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger or condenser and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the impingers or condenser. After wiping off the silicone grease, cap off the filter holder outlet and impinger inlet. Either ground glass stoppers or plastic caps or serum caps may be used to close these openings.

Transfer the probe and filter-impinger assembly to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

Save a portion of the acetone used for cleanup as a blank. Place about 200 ml of this acetone taken directly from the wash bottle being used in a glass sample container labeled "acetone blank."

Inspect the train prior to and during disassembly and note any abnormal conditions. Treat the samples as follows:

Container No. 1. Carefully remove the filter from the filter holder and place in its identified petri dish container. Use a pair of tweezers and/or clean disposable surgical gloves to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Quantitatively remove any particulate matter and/or filter which adheres to the filter holder gasket by carefully using a dry nylon bristle brush and/or a sharp-edged blade and place into this container. Seal the container.

Container No. 2. Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with acetone and placing the wash into a glass container in the following manner:

Distilled water may be used instead of acetone when approved by the Administrator or shall be used when specified by the Administrator. In these cases, save a water blank and follow Administrator's directions on analysis.

Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a nylon bristle brush. Brush until acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

Brush and rinse with acetone the inside parts of the Swagelok fitting in a similar way until no visible particles remain.

Rinse the probe liner with acetone by tilting the probe and squirting acetone into its upper end, while rotating the probe so that all inside surfaces will be rinsed with acetone. Let the acetone drain from the lower end into the sample container. A funnel may be used to aid in transferring liquid washes to the container. Follow the acetone rinse with a probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action through the probe, hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed from the probe. Run the brush through the probe three times or more until no visible particulate matter is carried out with the acetone or remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with acetone and quantitatively collect these washings in the sample container. After the brushing make a final acetone rinse of the probe as described above.

It is recommended that two people be used to clean the probe to minimize losing the sample. Between sampling runs, keep brushes clean and protected from contamination.

After ensuring that all joints are wiped clean of silicone grease, clean the inside of the front half of the filter holder by rubbing the surfaces with a nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. After all acetone washings and particulate matter are collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Label container to clearly identify its contents.

Container No. 3. Note color of indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from the fourth impinger to the original container and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the walls and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, follow the procedure under analysis.

Impinger water. Treat the impingers or condenser as follows: Make a notation of any color or film in the liquid catch. Measure the liquid which is in the first three impingers to within ±1 ml by using a graduated cylinder or, if available, to within ±0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

If analysis of the impinger catch is not required, discard the liquid after measuring and recording the volume or weight. If analysis of the impinger catch is required, leave the impingers intact to transfer the liquid, cap off the inlet, and pour the liquid through the outlet into the graduated cylinder or into a sample container after its weight has been determined.

If a different type of condenser is used, measure the amount of moisture condensed either volumetrically or gravimetrically.

4.3 Analysis. Record the data required on the example sheet shown in Figure 5-3. Handle each sample container as follows:

Container No. 1. Leave in shipping container or transfer the filter and any loose particulate from the sample container to a tared glass weighing dish and desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh to a constant weight and report the results to the nearest 0.1 mg. For purposes of this section 4.3, the term "constant weight" means a difference of no more than 0.5 mg or 1 percent of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings and no more than 2 minutes exposure to the laboratory atmosphere (must be less than 50 percent relative humidity) during weighing.

Plant ______________________

Date ______________________

Run No. ______________________

Relative Humidity ______________________

Amount liquid lost during transport ______________________

Acetone blank volume, ml ______________________

Acetone wash volume, ml ______________________

Acetune blank concentration, mg/mg (equation 5-4) ______________________

Acetone wash blank, mg (equation 5-5) ______________________

CONTAINER NUMBER	WEIGHT OF PARTICULATE COLLECTED, mg		
	FINAL WEIGHT	TARE WEIGHT	WEIGHT GAIN
1			
2			
TOTAL			
		Less acetone blank	
		Weight of particulate matter	

	VOLUME OF LIQUID WATER COLLECTED	
	IMPINGER VOLUME, ml.	SILICA GEL WEIGHT, g
FINAL		
INITIAL		
LIQUID COLLECTED		
TOTAL VOLUME COLLECTED		g* ml

CONVERT WEIGHT OF WATER TO VOLUME BY DIVIDING TOTAL WEIGHT INCREASE BY DENSITY OF WATER (1g/ml).

$$\frac{\text{INCREASE, g}}{\text{1 g/ml}} = \text{VOLUME WATER, ml}$$

Figure 5-3. Analytical data.

Container No. 2. Note level of liquid in container and confirm on analysis sheet whether or not leakage occurred during transport. Measure the liquid in this container either volumetrically to ±1 ml or gravimetrically to ±0.5 g. Transfer the contents to a tared 250 ml beaker, and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

Container No. 3. Weigh the spent silica gel to the nearest 0.5 g using a balance. This step may be conducted in the field.

"Acetone Blank" Container. Measure acetone in this container either volumetrically or gravimetrically. Transfer the acetone to a tared 250 ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

5. Calibration.

Maintain a laboratory log of all calibrations.

5.1 Probe nozzle. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make 3 separate measurements using different diameters each time and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.).

When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use.

Each nozzle shall be permanently and uniquely identified.

5.2 Pitot tube. The pitot tube shall be calibrated according to the procedure outlined in Method 2.

5.3 Dry gas meter and orifice meter. Both meters shall be calibrated according to the procedure outlined in APTD-0576. When a diaphragm pump is used, assure that there is no leak.

5.4 Probe heater calibration. The probe heating system shall be calibrated according to the procedure contained in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used.

5.5 Temperature gauges. Calibrate dial and liquid filled bulb thermometers and thermocouple-potentiometer systems against mercury-in-glass thermometers. Ice bath and boiling water (corrected for barometric pressure) are acceptable reference points. For other devices, check with the Administrator.

6. Calculations.

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

6.1 Nomenclature

A_n = Cross sectional area of nozzle, m² (ft²)
B_{ws} = Water vapor in the gas stream, proportion by volume
C_a = Acetone blank residue concentration, mg/g
c_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g/dscf)
I = Percent of isokinetic sampling
m_n = Total amount of particulate matter collected, mg
M_w = Molecular weight of water, 18 g/g-mole (18 lb/lb-mole)
m_a = Mass of residue of acetone after evaporation, mg
P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg)
P_s = Absolute stack gas pressure, mm Hg (in. Hg)
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg)
R = Ideal gas constant, 0.06236 mm Hg-m³/°K-g-mole (21.83 in. Hg-ft³/°R-lb-mole)
T_m = Absolute average dry gas meter temperature see (Figure 5-2), °K (°R)
T_s = Absolute average stack gas temperature (see Figure 5-2), °K (°R)
T_{std} = Standard absolute temperature, 293° K (528° R)
V_a = Volume of acetone blank, ml
V_{aw} = Volume of acetone used in wash, ml
V_{lc} = Total volume of liquid collected in impingers and silica gel (see Figure 5-3), ml
V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf)
$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter corrected to standard conditions, dscm (dscf)
$V_{w(std)}$ = Volume of water vapor in the gas sample corrected to standard conditions, scm (scf)
v_s = Stack gas velocity, calculated by Method 2, Equation 2-7 using data obtained from Method 5, m/sec (ft/sec)
W_a = Weight of residue in acetone wash, mg
ΔH = Average pressure differential across the orifice meter (see Figure 5-2), mm H_2O (in. H_2O)
ρ_a = Density of acetone, mg/ml (see label on bottle)
ρ_w = Density of water, 1 g/ml (0.00220 lb/ml)
θ = Total sampling time, min
13.6 = Specific gravity of mercury
60 = Sec/min
100 = Conversion to percent

6.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 5-2).

6.3 Dry gas volume. Correct the sample volume measured by the dry gas meter to standard conditions (20° C, 760 mm Hg or 68° F, 29.92 in. Hg) by using Equation 5-1.

$$V_{m(std)} = V_m\left(\frac{T_{std}}{T_m}\right)\left[\frac{P_{bar}+\frac{\Delta H}{13.6}}{P_{std}}\right[= K V_m \left[\frac{P_{bar}+\Delta H/13.6}{T_m}\right]$$

Equation 5-1

where:

K = 0.3855 °K/mm Hg for metric units

= 17.65 °R/in. Hg for English units

6.4 Volume of water vapor.

$$V_{w(std)}=V_{lc}\left(\frac{\rho_w}{M_w}\right)\left(\frac{RT_{std}}{P_{std}}\right)=KV_{lc}$$

Equation 5-2

where:

K=0.00134 m³/ml for metric units
=0.0472 ft³/ml for English units

6.5 Moisture content.

$$B_{ws}=\frac{V_{w(std)}}{V_{m(std)}+V_{w(std)}}$$

Equation 5-3

6.6 Acetone blank concentration.

$$C_a=\frac{m_a}{V_a\rho_a}$$

Equation 5-4

6.7 Acetone wash blank.

$$W_a=C_aV_{aw}\rho_a$$

Equation 5-5

6.8 Total particulate weight. Determine the total particulate catch from the sum of the weights obtained from containers 1 and 2 less the acetone blank (see Figure 5-3).

6.9 Particulate concentration.

$$c_s=(0.001\ g/mg)(m_n/V_{m(std)})$$

Equation 5-6

6.10 Conversion factors:

From—	To—	Multiply by—
scf	m³	0.0283
g/ft³	gr/ft³	15.4
g/ft³	lb/ft³	2.205×10^{-3}
g/ft³	g/m³	35.31

6.11 Isokinetic variation.

6.11.1 Calculations from raw data.

$$I=\frac{100T_s[KV_{lc}+(V_m/T_m)P_{bar}+\Delta H/13.6)]}{60\theta v_sP_sA_n}$$

Equation 5-7

where:

K=0.00346 mm Hg-m³/ml-°K for metric units

=0.00267 in. Hg-ft³/ml-°R for English units

6.11.2 Calculations from intermediate values.

$$I=\frac{T_sV_{m(std)}P_{std}100}{T_{std}v_s\theta A_nP_s60(1-B_{ws})}$$

$$=K\frac{T_sV_{m(std)}}{P_sv_sA_n\theta(1-B_{ws})}$$

Equation 5-8

where:

K=4.323 for metric units

=0.0944 for English units

6.12 Acceptable results. If 90 percent ≤I ≤110 percent, the results are acceptable. If the results are low in comparison to the standards and I is beyond the acceptable range, the Administrator may option to accept the results. Use reference 7.4 to make judgments. Otherwise, reject the results and repeat the test.

7. *Reference.*

7.1 Addendum to Specifications for Incinerator Testing at Federal Facilities, PHS, NCAPC, Dec. 6, 1967.

7.2 Martin, Robert M., Construction Details of Isokinetic Source Sampling Equipment, Environmental Protection Agency, APTD-0581, April 1971.

7.3 Rom, Jerome J., Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment, Environmental Protection Agency, APTD-0576, March 1972.

7.4 Smith, W. S., R. T. Shigehara, and W. F. Todd. A Method of Interpreting Stack Sampling Data, Paper presented at the 63d Annual Meeting of the Air Pollution Control Association, St. Louis, Mo., June 14-19, 1970.

7.5 Smith, W. S., et al., Stack Gas Sampling Improved and Simplified with New Equipment, APCA paper No. 67-119, 1967.

7.6 Specifications for Incinerator Testing at Federal Facilities, PHS, NCAPC, 1967.

7.7 Shigehara, R. T., Adjustments in the EPA Nomograph for Different Pitot Tube Coefficients and Dry Molecular Weights, Stack Sampling News 2:4-11, Oct. 1974.

METHOD 6—DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and Applicability.*

1.1 Principle. A gas sample is extracted from the sampling point in the stack. The acid mist (including sulfur trioxide) and the sulfur dioxide are separated. The sulfur dioxide fraction is measured by the barium-thorin titration method.

1.2 Applicability. This method is applicable for the determination of sulfur dioxide emissions from stationary sources. The minimum detectable limit of the method has been determined to be 3.4 mg of SO_2/m³ (2.1×10^{-7} lb/ft³). No upper limit has been established.

2. *Apparatus.*

2.1 Sampling. See Figure 6-1.

2.1.1 Probe—Borosilicate glass, approximately 5 to 6 mm ID, with a heating system to prevent water condensation and equipped with a filter (either in-stack or heated out-stack) to remove particulate matter including sulfuric acid mist.

2.1.2 Bubbler and impingers—One midget bubbler, with medium coarse glass frit and borosilicate or quartz glass wool packed in top (see Figure 6-1) to prevent sulfuric acid mist carryover; and three midget impingers, each with 30 ml capacity, or equivalent. The bubbler and midget impingers shall be connected in series with leak free glass connectors. Silicone grease may be used, if necessary, to prevent leakage.

2.1.3 Glass wool-Borosilicate or quartz.

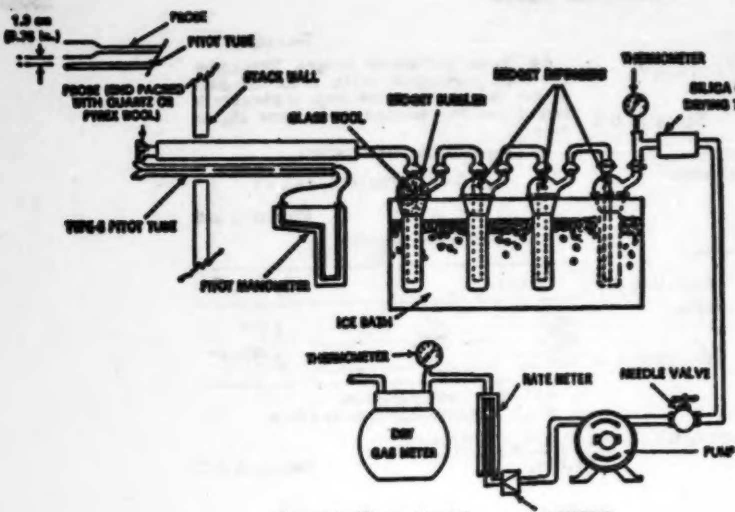

Figure 6-1. SO_2 sampling train.

2.1.4 Stopcock grease—Acetone insoluble, heat stable silicone grease may be used, if necessary.

2.1.5 Drying tube—Tube packed with 6 to 16 mesh indicating-type silica gel, or equivalent, to dry the gas sample and to protect the meter and pump.

2.1.6 Valve—Needle valve, to regulate sample gas flow rate.

2.1.7 Pump—Leak free diaphragm pump, or equivalent, to pull gas through the train.

2.1.8 Volume meter—Dry gas meter, sufficiently accurate to measure the sample volume within 2 percent, calibrated over the range of flow rates and conditions actually used during sampling and equipped with a temperature gauge (dial thermometer, or equivalent).

2.1.9 Flow Meter—Rotameter, or equivalent, to measure flow range from 0–3 lpm (0 to 6 cfh).

2.1.10 Pitot tube—Type S, or equivalent, attached to probe to allow constant monitoring of the stack gas velocity so that the sampling flow rate can be regulated proportional to the stack gas velocity. The tips of the probe and pitot tube shall be adjacent to each other and the free space between them shall be about 1.9 cm (0.75 in.). When used with this method, the pitot tube need not be calibrated.

The pitot tube shall be equipped with an inclined manometer, or equivalent device, capable of measuring velocity head to within 10 percent of the minimum measured value or ±0.013 mm (0.0005 in.), whichever is greater.

2.1.11 Temperature gauge—Dial thermometer, or equivalent, to measure temperature of gas leaving impinger train to within 1° C (2° F).

2.1.12 Barometer—Mercury, aneroid, or other barometers capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby weather bureau station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.1.13 Vacuum gauge—At least 760 mm Hg (30 in. Hg) gauge, to be used for the sampling train leak check.

2.2 Sample recovery.

2.2.1 Wash bottles—Polyethylene or glass, 500 ml, two.

2.2.2 Storage bottles—Polyethylene, 100 ml, to store impinger samples (one per sample).

2.3 Analysis.

2.3.1 Pipettes—Volumetric type, 5 ml size, 20 ml size (one per sample), and 25 ml size.

2.3.2 Volumetric flasks—100 ml size (one per sample) and 1000 ml sizes.

2.3.3 Burettes—5 ml and 50 ml sizes.

2.3.4 Erlenmeyer flasks—250 ml size (one for each sample, blank, and standard).

2.3.5 Dropping bottle—125 ml size, to add indicator.

2.3.6—Graduated cylinder—100 ml size.

3. *Reagents.*

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise use best available grade.

3.1 Sampling.

3.1.1 Water—Deionized, distilled to conform to ASTM specification D1193–72, Type 3.

3.1.2 Isopropanol, 80 percent—Mix 80 ml of isopropanol with 20 ml of deionized, distilled water.

3.1.3 Hydrogen peroxide, 3 percent—Dilute 30 percent hydrogen peroxide 1:9 (v/v) with deionized, distilled water (30 ml is needed per sample). Prepare fresh daily.

3.2 Sample recovery.

3.2.1 Water—Deionized, distilled, as in 3.1.1.

3.2.2 Isopropanol, 80 percent—Mix 80 ml of isopropanol with 20 ml of deionized, distilled water.

3.3 Analysis.

3.3.1 Water—Deionized, distilled, as in 3.1.1.

3.3.2 Isopropanol, 100 percent.

3.3.3 Thorin indicator—1-(o-arsonophenylazo)-2-naphtol-3, 6-disulfonic acid, disodium salt, or equivalent. Dissolve 0.20 g in 100 ml of deionized, distilled water.

3.3.4 Barium perchlorate solution, 0.01 N—Dissolve 1.95 g of barium perchlorate trihydrate [$Ba(ClO_4)_2 \cdot 3H_2O$] in 200 ml distilled water and dilute to 1 liter with isopropanol. $BaCl_2 \cdot 2H_2O$ (1.22 g) may also be used. Standardize as in section 5.2.

3.3.5 Sulfuric acid standard, 0.01 N—Purchase or standardize to ±0.0002 N against 0.01 N NaOH which has previously been standardized against potassium acid phthalate (primary standard grade).

4. *Procedure.*

4.1 Sampling.

4.1.1 Preparation of collection train. Measure 15 ml of 80 percent isopropanol into the midget bubbler and 15 ml of 3 percent hydrogen peroxide into each of the first two midget impingers. Leave the final midget impinger dry. Assemble the train as shown in Figure 6–1. Adjust probe heater to operating temperature. Place crushed ice and water around the impingers. Leak check the sampling train just prior to use at the sampling site by placing a vacuum gauge at the inlet to the first impinger and pulling a vacuum of at least 250 mm Hg (10 in. Hg), plugging or pinching off the outlet of the flowmeter, and then turning off the pump. The vacuum shall remain stable for at least one minute. Carefully release the vacuum gauge before releasing the flowmeter end. Connect the probe.

4.1.2 Sample collection. Record the initial dry gas meter reading and barometric pressure. To begin sampling, position the tip of the probe at the sampling point and start the pump. Adjust the sample flow to a rate of approximately 1 lpm as indicated by the rotameter. Sample at a rate that is proportional (within 20 percent of the average

$$V_m/\sqrt{\Delta P})$$

to the stack gas velocity throughout the run. Take readings (dry gas meter, temperatures at dry gas meter and at impinger outlet, rate meter, and velocity head) at least every five minutes and when significant changes (20 percent variation in velocity head readings) in stack conditions necessitate additional adjustments in sample flow rate. Add more ice during the run to keep the temperature of the gases leaving the last impinger at 20° C (68° F) or less. At the conclusion of each run, turn off the pump, remove probe from the stack, and record the final readings. Conduct a leak check as before. If excessive leakage rate is found void the test run. Remove the probe from the stack and disconnect it from the train. Drain the ice bath and purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the sampling rate.

Note.—Clean ambient air can be provided by passing air through a charcoal filter or through an extra midget impinger with 15 ml 3 percent H_2O_2. The tester may option to simply use the ambient air.

4.2 Sample recovery. Disconnect the impingers after purging. Discard the contents of the midget bubbler. Pour the contents of the midget impingers into a leak-free polyethylene bottle for shipment. Rinse the three midget impingers and the connecting tubes with deionized, distilled water and add the washings to the same storage container. Mark the fluid level. Seal and identify the sample container.

4.3 Sample analysis. Note level of liquid in container and confirm whether or not any sample was lost during shipment by noting this on analytical data sheet.

Note.—Protect the 0.01 N barium perchlorate solution from evaporation at all times.

Transfer the contents of the storage container to a 100 ml volumetric flask and dilute to exactly 100 ml with deionized, distilled water. Pipette a 20 ml aliquo of this solution into a 250 ml Erlenmeyer flask, add 80 ml of isopropanol, two to four drops of thorin indicator and titrate to a pink endpoint using 0.01 N barium perchlorate. Repeat and average the titration volumes. Run a blank with each series of samples. Replicate titrations shall agree within 1 percent.

5. *Calibration.*

5.1 Use methods and equipment as specified in Methods 2 and 5 and APTD–0576 to calibrate the rotameter, pitot tube, dry gas meter, barometer, and thermometers.

5.2 Standardize the barium perchlorate solution against 25 ml of standard sulfuric acid to which 100 ml of isopropanol has been added.

6. *Calculations.*

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

6.1 Nomenclature.

C_{SO_2} = Concentration of sulfur dioxide, dry basis corrected to standard conditions, mg/dscm (lb/dscf)
N = Normality of barium perchlorate titrant, milliequivalents/ml
P_{bar} = Barometric pressure at the exit orifice of the dry gas meter, mm Hg (in. Hg)
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg)
T_m = Average dry gas meter absolute temperature, °K (°R)
T_{std} = Standard absolute temperature, 293° K (528° R)
V_a = Volume of sample aliquot titrated, ml
V_m = Dry gas volume as measured by the dry gas meter, dcm (dcf)
$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf)
V_{soln} = Total volume of solution in which the sulfur dioxide sample is contained, 100 ml
V_t = Volume of barium perchlorate titrant used for the sample, ml (average of replicate titrations)
V_{tb} = Volume of barium perchlorate titrant used for the blank, ml
32.03 = Equivalent weight of sulfur dioxide

6.2 Dry sample gas volume, corrected to standard conditions.

$$V_{m(std)}=V_m\frac{T_{std}}{T_m}\frac{P_{bar}}{P_{std}}=K\frac{V_mP_{bar}}{T_m}$$

Equation 6-1

where:
K = 0.3855 °K/mm Hg for metric units
= 17.65 °R/in. Hg for English units

6.3 Sulfur dioxide concentration.

$$C_{SO_2}=K\frac{(V_t-V_{tb})N\left(\frac{V_{soln}}{V_a}\right)}{V_{m(std)}}$$

Equation 6-2

where:
K = 32.03 mg/meq. for metric units
$=7.05\times10^{-6}\frac{(lb)(l)}{(g)(ml)}$ for English units

7. *References.*

7.1 Atmospheric Emissions from Sulfuric Acid Manufacturing Processes, U.S. DHEW, PHS, Division of Air Pollution, Public Health Service Publication No. 999-AP-13, Cincinnati, Ohio, 1965.

7.2 Corbett, P. F., The Determination of SO_2 and SO_3 in Flue Gases, Journal of the Institute of Fuel, 24, 237-243, 1961.

7.3 Matty, R. E. and E. K. Diehl, Measuring Flue-Gas SO_2 and SO_3, Power 101:94-97, November 1957.

7.4 Patton, W. F. and J. A. Brink, Jr., New Equipment and Techniques for Sampling Chemical Process Gases, J. Air Pollution Control Association, 13, 162 (1963).

7.5 Rom, J. J., Maintenance, Calibration, and Operation of Isokinetic Source-Sampling Equipment. Office of Air Programs, Environmental Protection Agency, Research Triangle Park, N.C., March 1972. APTD-0576.

7.6 Hamil, H. F. and Camann, D. E., Collaborative Study of Method for the Determination of Sulfur Dioxide Emissions From Stationary Sources. Prepared for Methods Standardization Branch, Quality Assurance and Environmental Monitoring Laboratory, National Environmental Research Center, Environmental Protection Agency, Research Triangle Park, N.C. 27711.

7.7 Annual Book of ASTM Standards. Part 23; Water, Atmospheric Analysis. pp. 203-205. American Society for Testing and Materials, Philadelphia, Penna. (1972).

METHOD 7—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and Applicability.*

1.1 Principle. A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution, and the nitrogen oxides, except nitrous oxide, are measured colormetrically using the phenoldisulfonic acid (PDS) procedure.

1.2 Applicability. This method is applicable to the measurement of nitrogen oxides emitted from stationary sources. The range of the method has been determined to be 2 to 400 milligrams NO_x as No_2 per dry standard cubic meter without having to dilute the sample.

2. *Apparatus.*

2.1 Sampling (See Figure 7-1).

2.1.1 Probe—Borosilicate glass tubing sufficiently heated to prevent water condensation and equipped with a filter (either in-stack or heated out of stack) to remove particulate matter. Heating is unnecessary if the probe remains dry during the purging period.

2.1.2 Collection flask—Two-liter borosilicate, round bottom with short neck and 24/40 standard taper opening, protected against implosion or breakage.

2.1.3 Flask valve—T-bore stopcock connected to a 24/40 standard taper joint.

2.1.4 Temperature gauge—Dial-type thermometer, or equivalent, capable of measuring 1° C (2° F) intervals from −5 to 50° C (25 to 125° F).

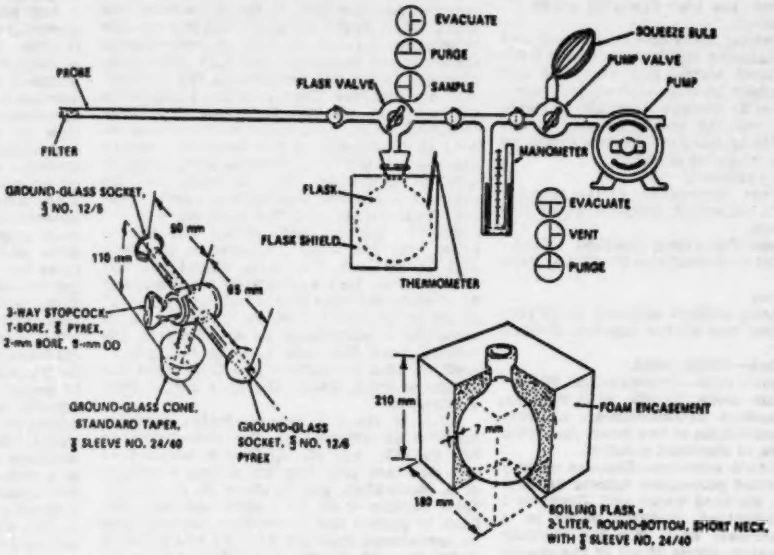
EVACUATE
PURGE
SAMPLE
SQUEEZE BULB
PUMP VALVE
PUMP
PROBE
FLASK VALVE
FILTER
MANOMETER
FLASK
FLASK SHIELD
THERMOMETER
EVACUATE
VENT
PURGE
GROUND-GLASS SOCKET, § NO. 12/5
90 mm
110 mm
65 mm
3-WAY STOPCOCK; T-BORE, § PYREX, 2-mm BORE, 9-mm OD
GROUND-GLASS CONE, STANDARD TAPER, § SLEEVE NO. 24/40
GROUND-GLASS SOCKET, § NO. 12/5 PYREX
210 mm
7 mm
FOAM ENCASEMENT
180 mm
BOILING FLASK - 2-LITER, ROUND-BOTTOM, SHORT NECK, WITH § SLEEVE NO. 24/40

Figure 7-1. Sampling train, flask valve, and flask.

2.1.5 Vacuum line—Tubing capable of withstanding a vacuum of 75 mm Hg (3 in. Hg) absolute pressure, with "T" connection and T-bore stopcock.

2.1.6 Pressure gauge—U-tube monometer, 1-meter, with 1-mm (36-in., with 0.1-in.) divisions, or equivalent.

2.1.7 Pump—Capable of evacuating the collection flask to a pressure equal to or less than 75 mm Hg (3 in. Hg) absolute.

2.1.8 Squeeze bulb—One-way

2.1.9 Volumetric pipette—25-ml.

2.1.10 Stopcock and ground joint grease—A high vacuum, high temperature chlorofluorocarbon grease is required. Halocarbon[1] 25-5S has been found to be effective.

2.1.11 Barometer—Mercury, aneroid, or other barometers capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby weather bureau station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.2 Sample recovery.

2.2.1 Graduated cylinder—50-ml with 1-ml divisions.

2.2.2 Storage container—Leak-free polyethylene bottles.

2.2.3 Wash bottle—polyethylene or glass.

2.2.4 Glass stirring rod.

2.2.5 pH indicating test paper—To cover the pH range of 7-14.

2.3 Analysis.

2.3.1 Volumetric pipettes—Two 1-ml, two 2-ml, one 3-ml, one 4-ml and two 10-ml, and one 25-ml for each sample and standard.

2.3.2 Porcelain evaporating dishes. 175 to 250-ml capacity with lip for pouring, one for each sample and each standard. The Coors[1] #45006 (shallow-form, 195 ml) has been found to be satisfactory.

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[1] Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

2.3.3 Steam bath. (A hot plate is not acceptable.)

2.3.4 Dropping pipette or dropper—Three required.

2.3.5 Polyethylene policeman—One for each sample and each standard.

2.3.6 Graduated cylinder—100-ml with 1-ml divisions.

2.3.7 Volumetric flasks—50-ml (one for each sample), 100-ml (one for each sample, each standard and one for the working standard KNO_3 solution), and one 1000-ml.

2.3.8 Spectrophotometer—To measure absorbance at 410 nm.

2.3.9 Graduated pipette—10-ml, with 0.1-ml divisions.

2.3.10 pH indicating test paper—To cover the pH range of 7–14.

2.3.11 Analytical balance—To measure to 0.1 mg.

3. *Reagents.*

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use best available grade.

3.1 Sampling.

3.1.1 Absorbing solution—Cautiously add 2.8 ml concentrated H_2SO_4 to 1 liter of deionized, distilled water. Mix well and add 6 ml of 3 percent hydrogen peroxide, freshly prepared from 30 percent hydrogen peroxide solution. The solution should be used within one week of its preparation. Do not expose to extreme heat or direct sunlight.

3.2 Sample recovery.

3.2.1 Sodium hydroxide (1N)—Dissolve 40 g NaOH in deionized, distilled water and dilute to 1 liter.

3.2.2 Water—Deionized, distilled to conform to ASTM specifications D1193–72, Type 3.

3.3 Analysis.

3.3.1 Fuming sulfuric acid—15 to 18 percent by weight free sulfur trioxide. Handle with caution.

3.3.2 Phenol—White solid.

3.3.3 Sulfuric acid—Concentrated, 95 percent minimum assay. Handle with caution.

3.3.4 Potassium nitrate—Dried at 105–110° C for a minimum of two hours just prior to preparation of standard solution.

3.3.5 Standard solution—Dissolve exactly 2.1980 g of dried potassium nitrate (KNO_3) in deionized, distilled water and dilute to 1 liter with deionized, distilled water in a 1000-ml volumetric flask. For the working standard solution, dilute 10 ml of the standard solution to 100 ml with deionized distilled water. One ml of the working standard solution is equivalent to 100 μg nitrogen dioxide (NO_2).

3.3.6 Water—Deionized, distilled as in section 3.2.2.

3.3.7 Phenoldisulfonic acid solution—Dissolve 25 g of pure white phenol in 150 ml concentrated sulfuric acid on a steam bath. Cool, add 75 ml fuming sulfuric acid, and heat at 100° C (212° F) for 2 hours. Store in a dark, stoppered bottle.

4. *Procedure.*

4.1 Sampling.

4.1.1 Pipette 25 ml of absorbing solution into a sample flask, retaining a sufficient quantity for use in preparing the calibration standards. Insert the flask valve stopper into the flask with the valve in the "purge" position. Assemble the sampling train as shown in figure 7–1 and place the probe at the sampling point. Make sure that all fittings are tight and leak free, and that all ground glass joints have been properly greased with a high vacuum, high temperature chlorofluorocarbon-based stopcock grease. Turn the flask valve and the pump valve to their "evacuate" positions. Evacuate the flask to 75 mm Hg (3 in. Hg) absolute pressure, or less. Evacuation to a lower pressure (approaching the vapor pressure of water at the existing temperature) is even more desirable. Turn the pump valve to its "vent" position and turn off the pump. Check for leakage by observing the manometer for any pressure fluctuation. (Any variation greater than 10 mm Hg (0.4 in. Hg) over a period of 1 minute is not acceptable, and the flask is not to be used until the leakage problem is corrected. Pressure in the flask is not to exceed 75 mm Hg (3 in. Hg) absolute at the time sampling is commenced.) Record the volume of the flask and valve (V_f), the flask temperature (T_i), and the barometric pressure. Turn the flask valve counterclockwise to its "purge" position and do the same with the pump valve. Purge the probe and the vacuum tube using the squeese bulb. If condensation occurs in the probe and the flask valve area, heat the probe and purge until the condensation disappears. Then turn the pump valve to its "vent" position. Turn the flask valve clockwise to its "evacuate" position and record the difference in the mercury levels in the manometer. The absolute internal pressure in the flask (P_i) is equal to the barometric pressure less the manometer reading. Immediately turn the flash valve to the "sample" position and permit the gas to enter the flask until pressures in the flask and sample line (i.e., duct, stack) are virtually equal. This will usually require about 15 seconds. A longer period indicates a "plug" in the probe which must be corrected before sampling is continued. After collecting the sample, turn the flask valve to its "purge" position and disconnect the flask from the sampling train. Shake the flask for at least 5 minutes.

4.1.2 If the gas being sampled contains insufficient oxygen for the conversion to NO to NO_2, e.g. an applicable subpart of the standard may require taking a sample of a calibration gas mixture of NO in N_2, then oxygen shall be introduced into the flask to permit this conversion. Oxygen may be introduced into the flask by one of three methods: (1) Before evacuating the sampling flask flush with pure cylinder oxygen (then evacuate flash to 75 mm Hg (3 in. Hg) absolute pressure or less); or (2) inject oxygen into the flask after sampling; or (3) sampling may be terminated with a minimum of 50 mm Hg (2 in. Hg) vacuum remaining in the flask, recording this final pressure and then venting the flask to the atmosphere until the flask pressure is almost equal to atmospheric pressure.

4.2 Sample recovery.

4.2.1 Let the flask set for a minimum of 16 hours and then shake the contents for 2 minutes. Connect the flask to a mercury filled U-tube manometer, open the valve from the flask to the manometer, and record the flash temperature (T_f), the barometric pressure and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask (P_f) is the barometric pressure less the manometer reading. Transfer the contents of the flask to a leak-free polyethylene bottle. Rinse the flask twice with 5-ml portions of deionized, distilled water and add the rinse water to the bottle. Adjust the pH to 9–12 by adding sodium hydroxide (1 N) dropwise (about 25 to 35 drops). Check the pH by dipping a stirring rod into the solution and then touching it to the pH test paper. Remove as little material as possible during this step. Mark the height of the liquid level to determine whether or not leakage occurred during transport. Label container to clearly identify its contents. Seal the container for shipping.

4.3 Analysis.

4.3.1 Note level of liquid in container and confirm whether or not any sample was lost during shipment by noting this on analytical data sheet. Transfer the contents of the shipping container to a 50-ml volumetric flask, rinse the container twice with 5-ml portions of deionized, distilled water, add the rinse water to the flask and dilute to the mark with deionized, distilled water. Mix thoroughly and pipette a 25-ml aliquot into the porcelain evaporating dish. Evaporate the solution to dryness on a steam bath and allow to cool. (Use only a steam bath—a hot plate is not acceptable.) Add 2 ml phenoldisulfonic acid solution to the dried residue and triturate thoroughly with a polyethylene policeman. Make sure the solution contacts all the residue. Add 1 ml deionized, distilled water and four drops of concentrated sulfuric acid. Heat the solution on a steam bath for 3 minutes with occasional stirring. Cool, add 20 ml deionized, distilled water, mix well by stirring and add concentrated ammonium hydroxide dropwise with constant stirring until pH is 10 (as determined by pH paper). If the sample contains solids, filter through Whatman No. 41 filter paper into a 100-ml volumetric flask; rinse the evaporating dish with three 5-ml portions of deionized, distilled water and add these to the filter. Wash the filter with at least three 15-ml portions of deionized, distilled water. Add the filter washings to the contents of the volumetric flask and dilute to the mark with deionized, distilled water. If solids are absent, transfer the solution directly to the 100-ml volumetric flask and dilute to the mark with deionized, distilled water. Mix thoroughly and measure the absorbance at 410 nm using the blank solution as a zero reference. Dilute the sample and the blank with a suitable amount of deionized, distilled water if absorbance exceeds A_4, the absorbance of the 400 μg NO_2 standard (See section 5.3).

5. *Calibration.*

5.1 Flask volume. Assemble the flask and flask valve and fill with water to the stopcock. Measure the volume of water to±10 ml. Number and record the volume on the flask.

5.2 Spectrophotometer calibration. Add 0.0 ml, 1.0 ml, 2.0 ml, 3.0 ml and 4.0 ml of the KNO_3 Working standard solution (1 ml=100 μg NO_2) to a series of five porcelain evaporating dishes. To each, add 25 ml of absorbing solution, 10 ml deionized, distilled water and sodium hydroxide (1 N) dropwise until the pH is 9–12 (about 25 to 35 drops each). Beginning with the evaporation step, follow the analysis procedure of Section 4.3 to collect the data necessary to calculate the calibration factor (Section 5.3). This calibration procedure must be repeated on each day that samples are analyzed.

5.3 Determination of spectrophotometer calibration factor K_c.

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[1] Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

$$K_c = 100 \frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2}$$

Equation 7-1

where:

K_c = Calibration factor
A_1 = Absorbance of the 100 μg NO_2 standard
A_2 = Absorbance of the 200 μg NO_2 standard
A_3 = Absorbance of the 300 μg NO_2 standard
A_4 = Absorbance of the 400 μg NO_2 standard

5.4 Barometer. Calibrate against a mercury barometer.

5.5 Temperature gauge. Calibrate dial thermometers against mercury-in-glass thermometers.

6. *Calculations.*

Carry out the calculations, retaining at lease one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

6.1 Nomenclature.

A = Absorbance of sample
C = Concentration of NO_x as NO_2, dry basis, corrected to standard conditions, mg/dscm (lb/dscf)
F = Dilution factor (i.e., 25/5, 25/10, etc, required only if sample dilution was needed to reduce the absorbance into the range of calibration)
K_c = Spectrophotometer calibration factor
m = Mass of NO_x as NO_2 in gas sample, μg
P_f = Final absolute pressure of flask, mm Hg (in. Hg)
P_i = Initial absolute pressure of flask, mm Hg (in. Hg)
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg)
T_f = Final absolute temperature of flask, °K (°R)
T_i = Initial absolute temperature of flask, °K (°R)
T_{std} = Standard absolute temperature, 293° K (528° R)
V_{sc} = Sample volume at standard conditions (dry basis), ml
V_f = Volume of flask and valve, ml
V_a = Volume of absorbing solution, 25 ml
2 = 50/25, the aliquot factor. (If other than a 25-ml aliquot was used for analysis, the corresponding factor must be substituted.)

6.2 Sample volume, dry basis, corrected to standard conditions.

$$V_{sc} = \frac{T_{std}}{P_{std}} (V_f - V_a) \left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right]$$

$$= K(V_f - 25 \text{ ml}) \left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right]$$

Equation 7-2

Where:

$$K = 0.3855 \frac{°K}{\text{mm Hg}} \text{ for metric units}$$

$$= 17.65 \frac{°R}{\text{in. Hg}} \text{ for English units}$$

6.3 Total μg NO_2 per sample.

$$m = 2K_cAF \quad \text{Equation 7-3}$$

NOTE.—If other than a 25-ml aliquot is used for analyses, the factor 2 must be substituted by a corresponding factor.

6.4 Sample concentration, dry basis, corrected to standard conditions.

$$C = K \frac{m}{V_{sc}} \quad \text{Equation 7-4}$$

where:

$$K = 10^3 \frac{(\text{ml})}{(\text{m}^3)} \frac{(\text{mg})}{(\mu\text{g})} \text{ for metric units}$$

$$= 6.243 \times 10^{-5} \frac{\text{lb/scf}}{\mu\text{g/ml}} \text{ for English units}$$

7. *References.*

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METHOD 8—DETERMINATION OF SULFURIC ACID MIST AND SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and Applicability.*

1.1 Principle. A gas sample is extracted isokinetically from the stack. The acid mist (including sulfur trioxide) and the sulfur dioxide are separated and both fractions are measured separately by the barium-thorin titration method.

1.2 Applicability. This method is applicable for the determination of sulfuric acid mist (including sulfur trioxide) in the absence of other particulate matter and for sulfur dioxide from stationary sources. Collaborative tests have shown that the minimum detectable limits of the method are 0.05 mg/m³ (0.03×10⁻⁷ lb/ft³) for sulfur trioxide and 1.2 mg/m³ (0.74×10⁻⁷ lb/ft³) for sulfur dioxide. No upper limits have been established.

2. *Apparatus*

2.1 Sampling. A schematic of the sampling train used in this method is shown in Figure 8-1; it is similar to the Method 5 train except that the filter position is different and heating of the filter holder is not required. Commercial models of this train are available. However, if one desires to build his own, complete construction details are described in APTD-0581; for changes from the APTD-0581 document and for allowable modifications to Figure 8-1, see the following subsections.

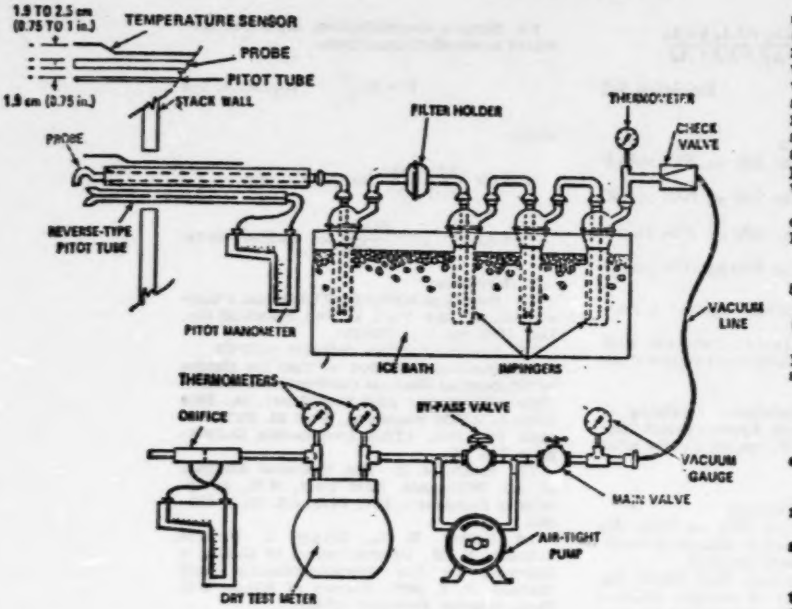

Figure 8 1. Sulfuric acid mist sampling train.

The operating and maintenance procedures for the sampling train are described in APTD-0576. Since correct usage is important in obtaining valid results, all users should read the APTD-0576 document and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein. Further details and guidelines on operation and maintenance are given in Method 5 and should be read and followed whenever they are applicable.

2.1.1 Probe nozzle—Stainless steel (316) with sharp, tapered leading edge. The angle of taper shall be ≤ 30° and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. The nozzle shall be constructed from seamless stainless steel tubing. Other configurations and construction material may be used with approval from the Administrator.

A range of sizes suitable for isokinetic sampling should be available, e.g., 0.32 cm (⅛ in.) up to 1.27 cm (½ in.) (or larger if higher volume sampling trains are used) inside diameter (ID) nozzles in increments of 0.16 cm (1/16 in.). Each nozzle shall be calibrated according to the procedures outlined in the calibration section.

2.1.2. Probe liner—Borosilicate or quartz glass, with a heating system to prevent visible condensation during sampling.

2.1.3 Pitot tube—Type S, or other device approved by the Administrator, attached to probe to allow constant monitoring of the stack gas velocity. The face openings of the pitot tube and the probe nozzle shall be adjacent and parallel to each other, not necessarily on the same plane, during sampling. The free space between the nozzle and pitot tube shall be at least 1.9 cm (0.75 in.). The free space shall be set based on a 1.3 cm (0.5 in.) ID nozzle. If the sampling train is designed for sampling at higher flow rates than that described in APTD-0581, thus necessitating the use of larger sized nozzles, the largest sized nozzle shall be used to set the free space.

The pitot tube must also meet the criteria specified in Method 2 and be calibrated according to the procedure in the calibration section of that method.

2.1.4 Differential pressure gauge—Inclined manometer capable of measuring velocity head to within 10 percent of the minimum measured value or ±0.013 mm (0.0005 in.), whichever is greater. Below a differential pressure of 1.3 mm (0.05 in.) water gauge, micromanometers with sensitivities of 0.013 mm (0.0005 in.) should be used. However, micromanometers are not easily adaptable to field conditions and are not easy to use with pulsating flow. Thus, methods or other devices acceptable to the Administrator may be used when conditions warrant.

2.1.5 Filter holder—Borosilicate glass with a glass frit filter support and a silicone rubber gasket. Other materials of construction may be used with approval from the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter.

2.1.6 Impingers—Four as shown in Figure 8-1. The first and third shall be of the Greenburg-Smith design with standard tips. The second and fourth shall be of the Greenburg-Smith design, modified by replacing the insert with an approximately 13 mm (0.5 in.) ID glass tube, having an unconstricted tip located 13 mm (0.5 in.) from the bottom of the flask. Similar collection systems, which have been approved by the Administrator may be used.

2.1.7 Metering system—Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3° C (5.4° F), dry gas meter with 2 percent accuracy, and related equipment, or equivalent, as required to maintain an isokinetic sampling rate and to determine sample volume. When the metering system is used in conjunction with a pitot tube, the system shall enable checks of isokinetic rates.

2.1.8 Barometer—Mercury, aneroid, or other barometers capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby weather bureau station, in which the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.1.9 Temperature gauge—Thermometer, or equivalent, to measure temperature of gas leaving impinger train to within 3° C (5° F).

2.2 Sample recovery.

2.2.1 Wash bottles—Polyethylene or glass, 500 ml. (two).

2.2.2 Graduated cylinders—250 ml, 1 liter. (Volumetric flasks may also be used.)

2.2.3 Storage bottles—Leak-free polyethylene bottles, 1000 ml size. (Two for each sampling run.)

2.3 Analysis.

2.3.1 Pipette—Volumetric 25 ml, 100 ml.

2.3.2 Burette—50 ml.

2.3.3 Erlenmeyer flask—250 ml. (One for each sample blank and standard.)

2.3.4 Graduated cylinder—100 ml.

2.3.5 Trip balance—300 g capacity, to measure to ±0.5 g.

2.3.6 Dropping bottle—to add indicator solution, 125 ml size.

3. *Reagents.*

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise use best available grade.

3.1 Sampling.

3.1.1 Filters—Glass fiber filters, without organic binder exhibiting at least 99.95 percent efficiency (≦0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordane with ASTM standard method D 2986-71. Test data from the supplier's quality control program is sufficient for this purpose.

3.1.2. Silica gel—Indicating type, 6-16 mesh. If previously used, dry at 175° C (350° F) for 2 hours. New silica gel may be used as received.

3.1.3 Water—Deionized, distilled, to conform to ASTM specifications D1193-72, Type 3.

3.1.4 Isopropanol, 80 percent—Mix 800 ml of isopropanol with 200 ml of deionized distilled water.

NOTE.—Experience has shown that only A.C.S. grade isopropanol is satisfactory.

3.1.5 Hydrogen peroxide, 3 percent—Dilute 100 ml of 30 percent hydrogen peroxide to 1 liter with deionized, distilled witer. Prepare fresh daily.

3.1.6 Crushed iced.

3.2 Sample recovery.

3.2.1 Water—Deionized, distilled, to conform to ASTM specifications D1193-72, Type 3.

3.2.2 Isopropanol, 80 percent—Mix 800 ml of isopropanol with 200 ml of deionized distilled water.

NOTE.—Experience has shown that only A.C.S. grade isopropanol is satisfactory.

3.3 Analysis.

3.3.1 Water—Deionized, distilled, to conform to ASTM specifications D1193-72, Type 3.

3.3.2 Isopropanol, 100 percent.

3.3.3 Thorin indicator—1-(o-arsonophenylazo)-2-naphthol-3, 6-disulfonic acid, disodium salt, or equivalent. Dissolve 0.20 g in 100 ml of deionized distilled water.

3.2.4 Barium perchlorate (0.01 N)—Dissolve 1.95 g of barium perchlorate trihydrate ($Ba(ClO_4)_2 \cdot 3H_2O$) in 200 ml deionized distilled water and dilute to 1 liter with isopropanol. Standardize with sulfuric acid as in Section 5.2. This solution must be protected against evaporation at all times. ($BaCl_2$ may also be used.)

3.2.5 Sulfuric acid standard (0.01 N)—Purchase or standardize to ±0.0002 N against 0.01 N NaOH which has previously been standardized against primary standard potassium acid phthalate.

4. *Procedure.*

4.1 Sampling.

4.1.1 Pretest preparation—Follow the procedure outlined in Method 5, Section 4.1.1, except that the filter need not be weighed or identified. If the effluent gas is considered to be dry, i.e., moisture free, the silica gel need not be weighed.

4.1.2 Preliminary determinations—Follow the procedure outlined in Method 5, Section 4.1.2.

4.1.3 Preparation of collection train—Follow the procedure outlined in Method 5, Section 4.1.2.

4.1.3 Preparation of collection train—Follow the procedure outlined in Method 5, Section 4.1.3, except for the second paragraph and use Figure 6-1 instead of Figure 5-1. Replace the second paragraph with: Place 100 ml of 80 percent isopropanol in the first impinger, 100 ml of 3 percent hydrogen peroxide in both the second and third impingers, and about 200 g of silica gel in the fourth impinger. Retain a portion of the reagents for use as blank solutions.

4.1.4 Leak-check procedure—Follow the procedure outlined in Method 5, Section 4.1.4, except that the probe heater shall be adjusted to the minimum temperature required to prevent condensation.

4.1.5 Train operation—Follow the procedure outlined in Method 5, Section 4.1.5, except record the data required on the example sheet shown in Figure 6-2. During the sampling period, observe the line between the probe and the first impinger for signs of condensation. If it occurs, adjust the probe heater setting upward to the minimum temperature required to prevent condensation. After turning off the pump and recording the final readings at the conclusion of each run, remove the probe from the stack and disconnect it from the train. Drain the ice bath and purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the average flow rate used for sampling.

NOTE.—Clean ambient air can be provided by passing air through a charcoal filter.

4.2 Sample recovery.

4.2.1 Container No. 1—Transfer the contents of the first impinger to a 250 ml graduated cylinder. Rinse the probe, first impinger, and all connecting glassware before the filter with 80 percent isopropanol. Add the rinse solution to the cylinder. Dilute to 250 ml with 80 percent isopropanol. Add the filter to the solution, mix, and transfer to the storage container. Protect the solution against evaporation. Mark the level of liquid on container and identify the sample container.

4.2.2 Container No. 2—Transfer the solutions from the second and third impingers to a 1000 ml graduated cylinder. Rinse all glassware between the filter and silica gel impinger with deionized, distilled water and add this rinse water to the cylinder. Dilute to a volume of 1000 ml with deionized, distilled water. Transfer the solution to a storage container. Mark the level of liquid on container. Seal and identify the sample container.

PLANT ____________
LOCATION ____________
OPERATOR ____________
DATE ____________
RUN NO. ____________
SAMPLE BOX NO. ____________
METER BOX NO. ____________
METER ΔH@ ____________
C FACTOR ____________
PITOT TUBE COEFFICIENT, Cp ____________

SCHEMATIC OF STACK CROSS SECTION

AMBIENT TEMPERATURE ____________
BAROMETRIC PRESSURE ____________
ASSUMED MOISTURE, % ____________
PROBE LENGTH, m (ft) ____________
NOZZLE IDENTIFICATION NO. ____________
AVERAGE CALIBRATED NOZZLE DIAMETER, cm (in.) ____________
PROBE HEATER SETTING ____________
LEAK RATE, m^3/min (cfm) ____________
PROBE LINER MATERIAL ____________

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	STATIC PRESSURE (P_S), mm Hg (in Hg)	STACK TEMPERATURE (T_S) °C (°F)	VELOCITY HEAD (ΔP_S).	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER mm H_2O (in. H_2O)	GAS SAMPLE VOLUME m^3 (ft^3)	GAS SAMPLE TEMPERATURE AT DRY GAS METER		TEMPERATURE OF GAS LEAVING CONDENSER OR LAST IMPINGER, °C (°F)
							INLET °C (°F)	OUTLET °C (°F)	
TOTAL							Avg.	Avg.	
AVERAGE							Avg.		

Figure 6-2. Field data.

4.3 Analysis.

Note level of liquid in containers 1 and 2 and confirm whether or not any sample was lost during shipment by noting this on analytical data sheet.

4.3.1 Container No. 1—Shake the container holding the isopropanol solution and the filter. If the filter breaks up, allow the fragments to settle for a few minutes before removing a sample. Pipette a 100 ml aliquot of this solution into a 250 ml Erlenmeyer flask, add 2 to 4 drops of thorin indicator, and titrate to a pink endpoint using 0.01 *N* barium perchlorate. Repeat the titration with a second aliquot of sample and average the titration values. Replicate titrations should agree within 1 percent.

4.3.2 Container No. 2—Throughly mix the solution in the container holding the contents of the second and third impingers. Pipette a 10 ml aliquot of sample into a 250 ml Erlenmeyer flask. Add 40 ml of isopropanol, 2 to 4 drops of thorin indicator, and titrate to a pink endpoint using 0.01 *N* barium perchlorate. Repeat the titration with a second aliquot of sample and average the titration values. Replicate titrations should agree within 1 percent.

4.3.3 Blanks—Prepare blanks by adding 2 to 4 drops of throin indicator to 100 ml of 80 percent isopropanol. Titrate the blanks in the same manner as the samples.

5. *Calibration.*

5.1 Use methods and equipment as specified in Methods 2 and 5 and APTD-0576 to calibrate the orifice meter, pitot tube, dry gas meter, thermometers, and barometer.

5.2 Standardize the barium perchlorate solution with 25 ml of standard sulfuric acid, to which 100 ml of isopropanol have been added.

6. *Calculations.*

NOTE.—Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

6.1 Nomenclature.

A_n = Cross sectional area of nozzle, m^2 (ft^2)
B_{ws} = Water vapor in the gas stream, proportion by volume
$C_{H_2SO_4}$ = Sulfuric acid (including SO_3) concentration, g/dscm (lb/dscf)
C_{SO_2} = Sulfur dioxide concentration, g/dscm (lb/dscf)
I = Percent of isokinetic sampling
N = Normality of barium perchlorate titrant, g. equiv/liter
P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg)
P_s = Absolute stack gas pressure, mm Hg (in. Hg)
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg)
T_m = Absolute average dry gas meter temperature (see Figure 8-2), °K (°R)
T_s = Absolute average stack gas temperature (see Figure 8-2), °K (°R)
T_{std} = Standard absolute temperature, 293° K (528° R)
V_a = Volume of sample aliquot titrated, 100 ml for H_2SO_4 and 10 ml for SO_2
V_{lc} = Total volume of liquid collected in impingers and silica gel (see Figure 8-2), ml
V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf)
$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter corrected to standard conditions, dscm (dscf)
v_s = Stack gas velocity, calculated by Method 2, Equation 2-7 using data obtained from Method 5, m/sec (ft/sec)
V_{soln} = Total volume of solution in which the sulfuric acid or sulfur dioxide sample is contained, 250 ml or 1000 ml, respectively
V_t = Volume of barium perchlorate titrant used for the sample, ml
V_{tb} = Volume of barium perchlorate titrant used for the blank, ml
θ = Total sampling time, min
13.6 = Specific gravity of mercury
60 = Sec/min
100 = Conversion to percent

6.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 8-2).

6.3 Dry gas volume. Correct the sample volume measured by the dry gas meter to standard conditions (20° C and 760 mm Hg or 68° F and 29.92 in. Hg) by using Equation 8-1.

$$V_{m(std)} = V_m \frac{T_{std}}{T_m} \frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}} = KV_m \frac{P_{bar} + \Delta H/13.6}{T_m}$$

Equation 8-1

where:

K = 0.3855 °K/mm Hg for metric units
= 17.65 °R/in. Hg for English units

6.4 Volume of water vapor and moisture content. Use Equation 5-2 and 5-3 of Method 5. If the effluent gas is considered to be dry, these calculations need not be carried out.

6.5 Sulfuric acid (including SO_3) concentration.

$$C_{H_2SO_4} = K \frac{N(V_t - V_{tb}) \frac{V_{soln}}{V_a}}{V_{m(std)}}$$

Equation 8-2

where:

K = 0.04904 g/milliequivalent for metric units
$= 1.08 \times 10^{-4} \frac{(lb)\ (l)}{(g)\ (ml)}$ for English units

6.6 Sulfur dioxide concentration:

$$C_{SO_2} = K \frac{N(V_t - V_{tb}) \frac{V_{soln}}{V_a}}{V_{m(std)}}$$

Equation 8-3

where:

K = 0.03203 g/milliequivalent for metric units
$= 7.05 \times 10^{-5} \frac{(lb)(l)}{(g)(m)}$ for English units

6.7 Isokinetic variation.

6.7.1 Calculations from raw data.

$$I = \frac{100T_s[KV_{lc} + (V_m/T_m)(P_{bar} + \Delta H/13.6)]}{60\theta V_s P_s A_n}$$

Equation 8-4

where:

K = 0.00346 mm Hg-m^3/ml-°K for metric units
= 0.00267 in. Hg-ft^3/ml-°R for English units

6.7.2 Calculations from intermediate values.

$$I = \frac{T_s V_{m(std)} P_{std} 100}{T_{std} v_s \theta A_n P_s 60(1 - B_{ws})}$$

$$= K \frac{T_s V_{m(std)}}{P_s v_s A_n \theta (1 - B_{ws})}$$

Equation 8-5

where:

K = 4.323 for metric units
= 0.0944 for English units

6.8 Acceptable results. If 90 percent ≤ I ≤ 110 percent, the results are acceptable. If the results are low in comparison to the standards and I is beyond the acceptable range, the Administrator may option to accept the results. Use reference 7.4 of Method 5 to make judgments. Otherwise, reject the results and repeat the test.

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APPENDIX D

PROCEDURE FOR CONING AND QUARTERING SOLID SAMPLES

D.1 INTRODUCTION

This procedure is an adaptation of ANSI/ASTM procedure 346-78, Standard Method of Sampling Coke for Analysis, which is hereby included as a reference.

D.2 SCOPE AND APPLICATION

This procedure applies to the acquisition of solid samples in the field, preparing field samples for shipment by coning and quartering, and any subsequent treatment in the laboratory prior to analysis. Typical solid samples requiring use of this procedure are fly ash, bottom ash, scrubber input materials, and coal feed.

The most preferable method of sample acquisition is by use of a plant's automic sampling system. If there is no automatic system for a required sample, time-integrated grab samples will be taken by shovel. Coning and quartering will be used to produce a representative sample for shipment to the laboratory and for reducing the size of samples in the laboratory.

D.3 APPARATUS

- Standard shovel, square edged, 12-inches wide
- Specified sample containers
- Clean Teflon sheet (for laboratory)
- Laminar flow bench (for laboratory)

D.4 REAGENTS

None

D.5 PROCEDURES

D.5.1 Automatic Sampling

Many plants are equipped with automatic samplers on process input streams. The units are calibrated to remove representative cross sections of a stream while automatically forming a homogeneous composite. Whenever these units are available, the sampling team should make use of them in preference to the shovel technique in Section D.5.2.

D.5.2 Fractional Shovel Grab Sampling

Fractional shoveling involves the acquisition of a time-integrated grab sample representative of overall process input or output during a given run time period. This procedure uses a standard square edged shovel, 12 inches wide. For streams in motion, either entering or exiting a process operation, a sample is taken from the belt on an hourly basis. A full cross-stream cut should be taken. Each hourly shovel sample is added to a pile to form eventually a composite for the entire test period. At the conclusion of the run, this pile will be coned and quartered (as described below in Section D.5.4) to form a final representative sample weighing from 2.3 to 4.5 kilograms (5 to 10 pounds).

It is always preferable to sample a moving stream rather than a stationary storage pile. This is particularly true if a large particle or lump size distribution exists in the material. Stored containers or heaped beds of material tend to settle, creating segregation of particles according to size and density, and it is more difficult to account for this bias in the sampling. If it becomes necessary to sample a stationary pile, every attempt should be made to acquire a fully representative sample by taking a number of grab samples from a variety of different areas and depths in the pile. A scheme for sampling stationary piles is given in the referenced ANSI/ASTM procedure.

D.5.3 Coning and Quartering

After a suitable composite sample has been acquired, a reparesentative sample for laboratory analysis must be removed. The usual method of accomplishing this task involves the coning and quartering technique.

The coning and quartering procedure involves the following 6 steps:

1) The material is first mixed and formed into a neat cone.
2) The cone is flattened by pressing the top without further mixing.
3) The flat circular pile is then divided into four quarters.
4) The two opposing quarters are discarded.
5) The two remaining quarters are mixed and steps 1-5 are repeated until a 5-10 pound laboratory sample is obtained.

6) The 5-10 pound laboratory sample is to be placed in a 1-gallon wide-mouthed polypropylene bottle, or other suitable containers.

D.6 REFERENCES

ANSI/ASTM 346-78. Standard Method of Sampling Coke for Analysis. Annual ASTM standards, Part 26, p. 213, 1978.

APPENDIX E

XAD-2 RESIN CLEANING PROCEDURE

E. CLEANING PROCEDURE FOR THE XAD-2 RESIN

The resin as supplied by the manufacturer is impregnated with a bicarbonate solution to inhibit microbial growth during storage. The salt solution as well as extractable organic species must be removed by the cleaning procedure prior to use as a sorbent agent. Purification of the resin is accomplished by a series of extractions employing three different solvents.

E.1 EXTRACTION APPARATUS

The continuous extractor fabricated for the extraction process is shown in Figure E-1. The resin container is constructed from a 3-liter resin kettle and accommodates ~800 g of resin. All materials of construction are glass, Teflon or stainless steel to maintain as low a level of contamination as possible. A coarse glass frit is placed at the bottom of the extractor to support the resin and at the same time allow for even distribution of the freshly distilled solvent. The distillation pot is a 5-liter flask and is equipped with a column, distillation head and condenser. During the extraction process, solvent is distilled and continuously cycled up through the XAD-2 resin for extraction and returned to the distillation flask through the Teflon line as shown in the diagram. Flow is from the bottom to the top in the extractor to allow maximum solvent contact and prevent channeling. Washing with water is performed employing a reversed flow. Water is added to the top of the extractor and allowed to drain out the bottom. The reversed flow is necessary because of the wetting characteristics of the resin. After extraction of the resin with the organic solvents (methanol and methylene chloride), the resin is dried using a stream of nitrogen. No heat is employed in the drying process.

E.2 OPERATING PROCEDURES

E.2.1 Water Wash

Add sufficient XAD-2 resin to fill the extractor to within ~1/2 inch of the top of the main body. Attach the resin kettle top to extractor body and evenly tighten clamps. Attach water line from reservoir (5 gal.) so that water enters the extractor at the top and flows out the bottom (Figure E-1).

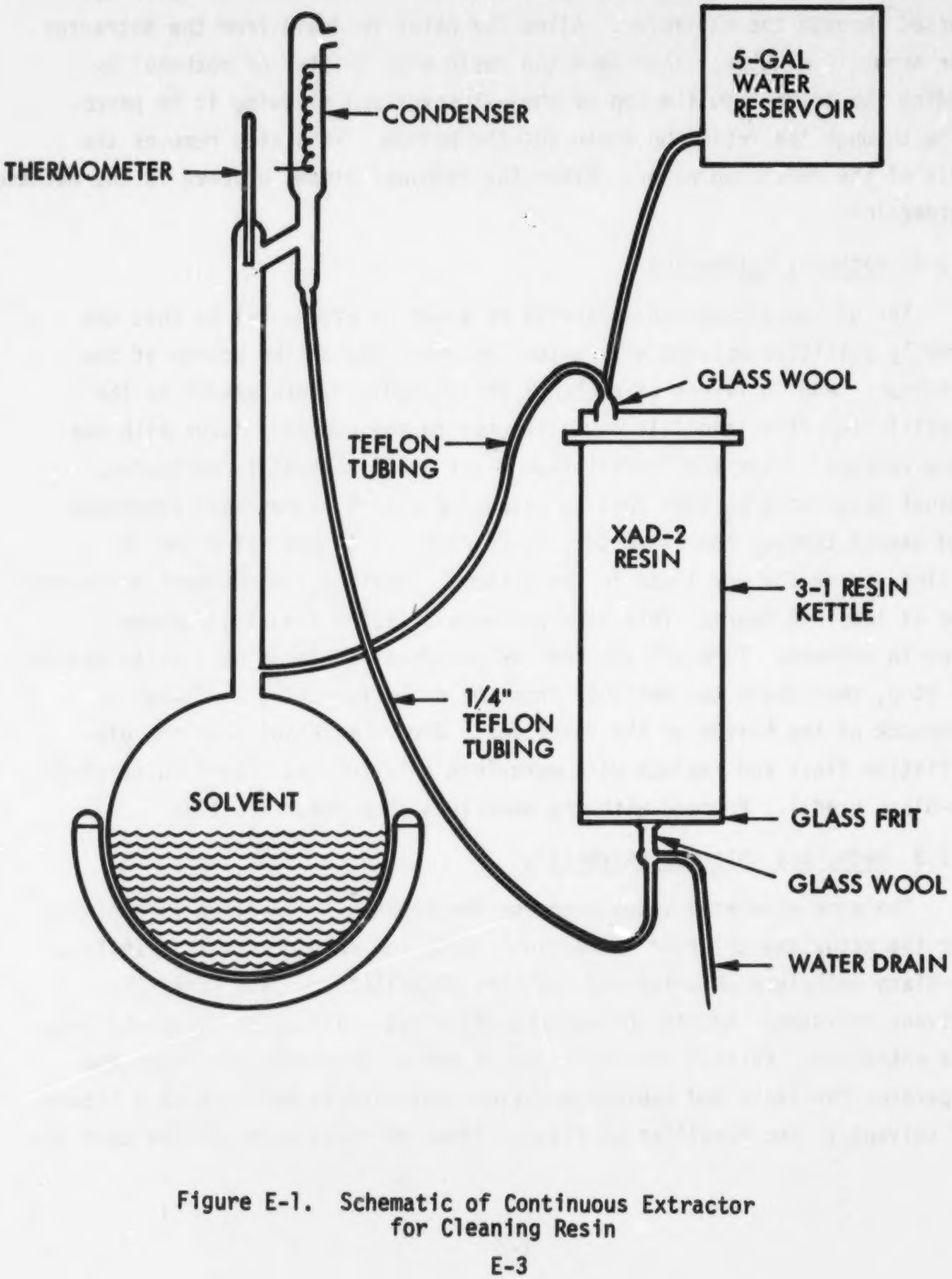

5-GAL
WATER
RESERVOIR
CONDENSER
THERMOMETER
GLASS WOOL
TEFLON
TUBING
XAD-2
RESIN
3-1 RESIN
KETTLE
1/4"
TEFLON
TUBING
SOLVENT
GLASS FRIT
GLASS WOOL
WATER DRAIN

Figure E-1. Schematic of Continuous Extractor for Cleaning Resin

Fill the reservoir with 5 gallons of deionized water, then start addition of water to the extractor. Adjust water flow out of extractor using the stopcock so that the resin is thoroughly wetted. The flow rate should be ∿100 ml/min. Continue washing until a total of 10 gallons of water has passed through the extractor. Allow the water to drain from the extractor for about 10 minutes. Then wash the resin with 1-liter of methanol by adding the solvent to the top of the extractor and allowing it to percolate through the resin and drain out the bottom. This step removes the bulk of the remaining water. After the methanol rinse, proceed to the methanol extraction.

E.2.2 Methanol Extraction

Set up the extraction apparatus as shown in Figure E-1 so that the freshly distilled solvent will enter the resin bed at the bottom of the canister. Add ∿3 liters of methanol (Distilled-in-Glass grade) to the distillation flask and fill the extractor to the body/top joint with the same solvent. Heat the distillation flask until solvent is refluxing. Adjust heat input so that boil-up rate, the amount of methanol condensed and passed through the extractor, is 20 ml/min. As the extractor is filled, check for any leaks in the system. Continue the methanol extraction for at least 16 hours. This time period will allow a sixfold changeover in solvent. Turn off the heat on the distillation flask, allow reflux to stop, then drain the methanol from the extractor using the 3-way stopcock at the bottom of the extractor. Remove methanol from the distillation flask and replace with methylene chloride (∿3 liters, Distilled-in-Glass grade). Proceed with the methylene chloride extraction.

E.2.3 Methylene Chloride Extraction

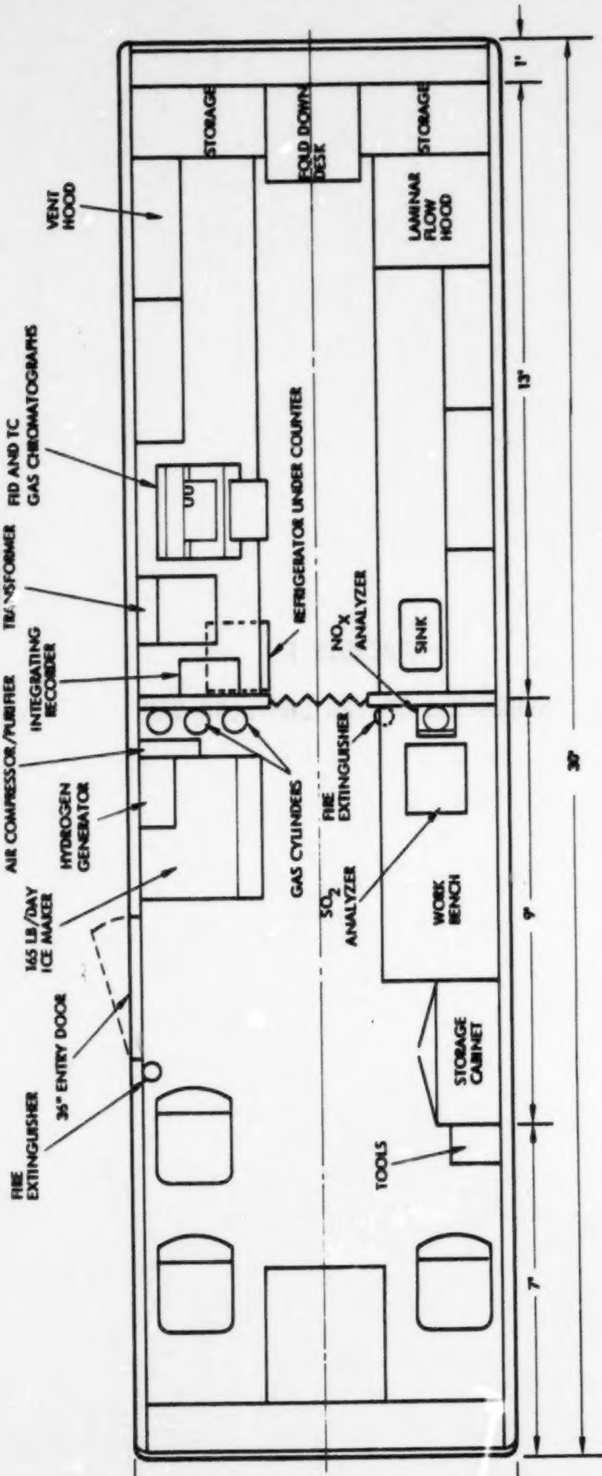
The same apparatus setup used for the methanol extraction is employed for the methylene chloride extraction. Fill the extractor with Distilled-in-Glass methylene chloride and heat the distillation flask until the solvent refluxes. Adjust boil-up rate to provide a flow of 15 ml/min into the extractor. Extract the resin for 24 hours. Periodically check the apparatus for leaks and replace methylene chloride to maintain ∿2.5 liters of solvent in the distillation flask. After 24 hours turn off the heat for the distillation flask and drain the solvent from the extractor through the 3-way stopcock.

E.2.4 Drying XAD-2 Resin

Connect a gas line (Teflon is preferred) from a nitrogen cylinder to the bottom of the extractor. This line is to be equipped with a tube containing clean XAD-2 resin to trap any organic components present in the nitrogen stream to prevent contamination of the purified resin. Remove two stoppers from the resin kettle top and start a slow flow of nitrogen through the resin. Periodically adjust the rate of gas flow so that the extractor and resin bed do not become supercooled during the drying step. Complete drying requires 24 to 48 hours and consumes a full cylinder of nitrogen. The dried resin is transferred to a clean bottle and sealed. Four batches are mixed together in the holding vessel to provide a lot of resin. Mixing is best accomplished by rolling the container of resin on a roller for ∿30 minutes. Each lot of resin must pass quality control tests for volatile and nonvolatile organic content before being bottled for use in the field. After quality control testing, cleaned resin is packed into the bottles; the bottles are filled with distilled, deionized water; and the bottles are sealed. Each bottle contains sufficient resin to fill one SASS train resin canister.

APPENDIX F

SCHEMATIC OF TRW SAMPLING VAN



FIRE EXTINGUISHER
35" ENTRY DOOR
165 LB/DAY ICE MAKER
AIR COMPRESSOR/PURIFIER
HYDROGEN GENERATOR
INTEGRATING RECORDER
ISOLATION TRANSFORMER
FID AND TC GAS CHROMATOGRAPHS
VENT HOOD
STORAGE
FOLD DOWN DESK
STORAGE
LAMINAR FLOW HOOD
REFRIGERATOR UNDER COUNTER
GAS CYLINDERS
FIRE EXTINGUISHER
NO_X ANALYZER
SINK
SO_2 ANALYZER
WORK BENCH
STORAGE CABINET
TOOLS
1'
13'
30'
9'
7'
8'

Figure F-1. Schematic of TRW Sampling Van